OCT 22 '43

UNITED STATES DEPARTMENT OF COMMERCE

Journal of Research

of the

National Bureau of Standards

Vol. 31, No. 4 October 1943

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Journal of Research

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Volume 31, Number 4

October 1943

[Published with approval of the Director of the Budget]

UNITED STATES
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MATHEMATICAL TABLES

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1558

Part of Journal of Research of the National Bureau of Standards, Volume 31, October 1943

THE ASSAY OF POTASSIUM *p*-PHENOLSULFONATE, ITS pH RANGE, AND ITS ULTRAVIOLET ABSORPTION SPECTRUM

By Elizabeth E. Sager, Marjorie R. Schooley, and S. F. Acree

ABSTRACT

Potassium *p*-phenolsulfonate is a good buffer for the pH range of 8.4 to 9.2 and for spectrophotometric studies of metacresolsulfonphthalein and thymolsulfonphthalein. Its useful pH range lies between those for borates and secondary phosphates and therefore fills an important gap. The purified product is not commercially available and quantitative tests for indicating its purity have not been reported. It was found that a pure product may be obtained after only three recrystallizations. A quantitative method of analysis by bromometric titration was developed. Two molecules of bromine react quantitatively with 1 molecule of *p*-phenolsulfonate in molar hydrochloric acid at 0° C within 5 minutes.

Ultraviolet absorption spectra were obtained and showed differences between the primary and the secondary salt. The spectrophotometric data indicate that the sulfonate group is almost completely ionized in dilute solutions.

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I. INTRODUCTION

In spectrophotometric studies of indicators it is sometimes necessary to use buffers to stabilize the solutions which cover the pH and colorimetric transformation ranges. It is especially important that the compounds used as buffers and the indicators do not react or have overlapping absorption bands. The phenolsulfonates and some of their halogenated derivatives have been suggested [1] as components of a stable buffer system over a wide pH range.

Highly purified phenolsulfonates are not available commercially. However, some of the compounds can be easily recrystallized from water and hence can be purified in the laboratory. After preliminary investigations of the potassium, sodium, calcium, and zinc salts of *p*-phenolsulfonic acid and of several salts of halogenated derivatives, potassium *p*-phenolsulfonate was chosen for more detailed study. The fact that it is anhydrous makes it more desirable than the sodium salt. The latter crystallizes with 2 molecules of water, which can be removed by drying but are taken up again at room temperature at

[1] S. F. Acree, R. R. Mellon, B. M. Avery, and E. A. Slagle, *A stable single buffer solution* pH *1 to 12*. J. Infectious Diseases **29**, 7 to 10 (1921).

humidities as low as 40 and 50 percent. Two samples of the recrystallized potassium salt lost 0.02 and 0.03 percent in weight when heated at 110° C for 24 hours and regained about the same amount over a period of 10 days, during which they were exposed from time to time in air of 40- to 50-percent humidity. Bromometric assay, by the procedure described later, showed no change in purity of the samples heated at 110° C for 24 hours. The same was true of a 10^{-2} molar solution which stood on the laboratory bench for 2 months. After heating at about 167° C for 20 hours, however, three samples lost 0.30 to 0.36 percent in weight and were found to contain sulfate. Bromometric analysis showed these samples to be 99.7 percent pure.

There apparently is no oxidation-reduction or other adverse reaction with the sulfonphthalein indicator series, as indicated by spectrophotometric curves, using 10^{-2} molar potassium *p*-phenolsulfonate buffers with metacresolsulfonphthalein and thymolsulfonphthalein.

II. PURIFICATION OF POTASSIUM *p*-PHENOLSULFONATE

The *p*-phenolsulfonate received from the manufacturer was a pinkish-white crystalline powder with a distinct phenolic odor. Impurities were removed before the first crystallization by treating a hot solution for about 10 minutes with an activated carbon. To remove all the carbon, the solution was filtered several times while hot. Each recrystallization was made by adding just enough hot water (about 80° to 90° C) to dissolve the crystals. The solution was then cooled to about 10° C, and the crystals were filtered with suction but not allowed to dry between recrystallizations. A yield of about 40 percent for each recrystallization was obtained. The first mother liquor was pinkish and contained a small amount of sulfate. The subsequent mother liquors were colorless and sulfate tests were negative.

Two separate lots of potassium *p*-phenolsulfonate were recrystallized four and six times, respectively. Some material from each recrystallization was reserved for experimentation and dried for 2 hours in a vacuum oven at 2-mm pressure and 60° C. Analyses of the recrystallized product by micromethods for hydrogen, carbon, and sulfur, made by K. D. Fleischer of this Bureau, gave the following results: Found: C, 34.02, 34.03; H, 2.40, 2.57; S, 14.92, 15.04. Theoretical: C, 33.95; H, 2.37; S, 15.10.

III. BROMOMETRIC ASSAY OF POTASSIUM *p*-PHENOLSULFONATE

Previous work on furfural and related compounds [2] showed that under controlled conditions of acidity and temperature the reaction of bromine with some organic compounds can be used as a method for their quantitative determination. Preliminary experiments indicated that the reaction of bromine with phenolsulfonate gives slightly high results at room temperature. However, using essentially the method previously reported for furfural, it was found that at 0° C 2 molecules of bromine react within 5 to 10 minutes with 1 molecule of *p*-phenolsulfonate in normal hydrochloric acid to form 2,6-dibromophenol-4-sulfonate and 2 molecules of hydrobromic acid. The reagents used and experimental procedure are given below.

[2] Elizabeth E. Hughes and S. F. Acree, *Quantitative determination of furfural at 0° C with bromine*, Ind Eng. Chem. **6**, 123 (1934); *Volumetric estimation of 5-bromo-2-furoic acid with bromine*, Ind. Eng. Chem. **6**, 222 (1934).

1. REAGENTS

Potassium bromate was recrystallized three times from water, and 5.567 g was used to make a solution approximately 0.2 *N*, which contained 50 g of potassium bromide in 1 kg of water. The bromate-bromide solution was used on a weight basis to standardize in normal hydrochloric acid through iodine the 0.1 *N* thiosulfate solution used for the titrations. The weighed amount of the bromate-bromide delivered by a special 25-ml pipet with curved tip was reproducible within 0.05 percent. A solution of potassium iodide, about 10 percent by weight, was prepared freshly before use. Hydrochloric acid was used to make the reacting solution about normal in acidity. The potassium bromide, potassium iodide, and hydrochloric acid conformed to specifications of the American Chemical Society.[3] As an additional check, the thiosulfate was standardized against potassium dichromate, recrystallized twice, using the same procedure described below. The two methods of standardization agreed within 0.1 percent.

2. EXPERIMENTAL PROCEDURE

Specially designed titration flasks, described previously (see footnote 2), were fitted with two side-arms for the bromate and iodide solutions, respectively. By means of pipets with curved tips, 25 ml of the 0.2 *N* bromate-bromide solution was placed in one side-arm and 10 ml of the potassium iodide solution in the other. A known amount of phenolsulfonate was transferred to the body of the flask and diluted to about 200 ml. The solution was made normal in acidity by the addition of hydrochloric acid, using extreme care that the fumes did not reach the bromate in the side-arm. Blanks of the reagents were prepared in a similar manner, substituting water for the phenolsulfonate. Each flask was closed with a ground-glass stopper and placed in an icebox to attain a temperature of 0° to 2° C.

The reaction was started by tilting the flask so that the bromate-bromide solution ran into the body of the flask, and the contents were gently swirled to mix the liberated bromine with the phenolsulfonate without disturbing the potassium iodide solution in the other side-arm. A stop watch was used to time the reaction, which was stopped by the addition of the potassium iodide. The contents were thoroughly shaken to absorb any bromine vapors, and the iodine equivalent to the residual bromine was titrated with 0.1 *N* thiosulfate, using starch as an indicator. At 0° C the discharge of the blue color at the end point was very definite, but it was found that the titration must be made as rapidly as possible. The blue color returns after several minutes, and consequently error may be introduced if the titration is prolonged. Experiments over a period of several hours, in which the blue color was discharged with thiosulfate as soon as it returned, showed that this error was of the order of 0.01 ml per minute at low temperatures and twice this amount at room temperatures.

The amount of bromine consumed by the phenolsulfonate is determined from the difference between the amounts of standard thiosulfate solution used in titrating the blank and the solution containing the phenolsulfonate. The figures in table 1 for "percent reaction" are calculated on the assumption that in the desired reaction 1 mole of the phenolsulfonate consumes 2 moles of bromine.

[3] ACS Analytical Reagents. (American Chemical Society, Washington, D. C., March 1941).

TABLE 1.—*Reaction of potassium p-phenolsulfonate with bromine at 0° C in normal hydrochloric acid*

Time allowed for reaction	0.1698 g of potassium p-phenolsulfonate		0.2124 g of potassium p-phenolsulfonate	
	Milliequivalents of bromine consumed	Percentage of reaction	Milliequivalents of bromine consumed	Percentage of reaction
Minutes				
2	----------	----------	{ 3.937	98.4
			{ 3.922	98.0
5	3.195	99.9	4.001	100.0
10	{ 3.199	100.0	4.006	100.1
	{ 3.200	100.0	4.002	100.0
15	3.199	100.0	{ 4.004	100.0
			{ 4.009	100.1
20	{ 3.205	100.1	----------	----------
	{ 3.207	100.2	----------	----------
30	3.210	100.2	----------	----------
120	3.256	101.8	4.025	100.6
180	----------	----------	4.038	100.9

The values in table 1 show the variation with time in the consumption of bromine at 0° C by two concentrations of phenolsulfonate. In all cases there were approximately 5.0 milliequivalents of bromine available, requiring 50 ml of 0.1 N thiosulfate for titration of the blank. For the above amounts of phenolsulfonate, the excess bromine required about 18 and 10 ml of thiosulfate, respectively. The table indicates that the reaction of 1 molecule of phenolsulfonate with 2 molecules of bromine is complete after about 5 minutes, and little additional reaction is noted until after 30 minutes. The figures for percentage of reaction show that the method is accurate to about 0.1 percent. A difference of 0.02 ml in thiosulfate titration, representing in the above instances less than 0.1 percent, is possible due to the difference in time taken to add the 50 ml for titration of the blank and that taken to add the smaller volume in the titration of the sample.

The values in table 2 show the analyses of the original material and the recrystallized fractions.

TABLE 2.—*Bromometric assay of samples of potassium p-phenolsulfonate subjected to a series of recrystallizations*

	First lot	Second lot
	Percent	*Percent*
Original material	92.8	92.7
Recrystallization I	98.4	99.6
Recrystallization II	99.7	100.0
Recrystallization III	100.0	100.1
Recrystallization IV	100.0	100.0
Recrystallization V	-----	100.1
Recrystallization VI	-----	100.1

IV. SPECTRAL ABSORPTION IN THE ULTRAVIOLET BY POTASSIUM *p*-PHENOLSULFONATE

In the spectrophotometric studies of indicators stabilized with 10^{-2} molar phenolsulfonate buffer, it was found that ultraviolet absorption spectra could not be obtained below 280 mμ, owing to the absorption bands of the buffer itself. A study therefore was made of the buffer without the indicator. Repeated dilutions of the phenol-

sulfonate solutions were made and their transmittancy values measured until the main absorption bands were located. The series of spectral transmittancy values given in figure 1 represent concentrations of the phenolsulfonate in water from 10^{-2} molar (curve *A*) to 10^{-5} molar (curve *I*). The main absorption band, whose peak is at 230 mμ, is not sharply defined except in the more dilute solutions (curves *E* through *I*). The transmittancy curves show bands similar to those of indicators.

Dilution of the phenolsulfonate with water immediately introduces the question of dissociation. At any wavelength the molar absorp-

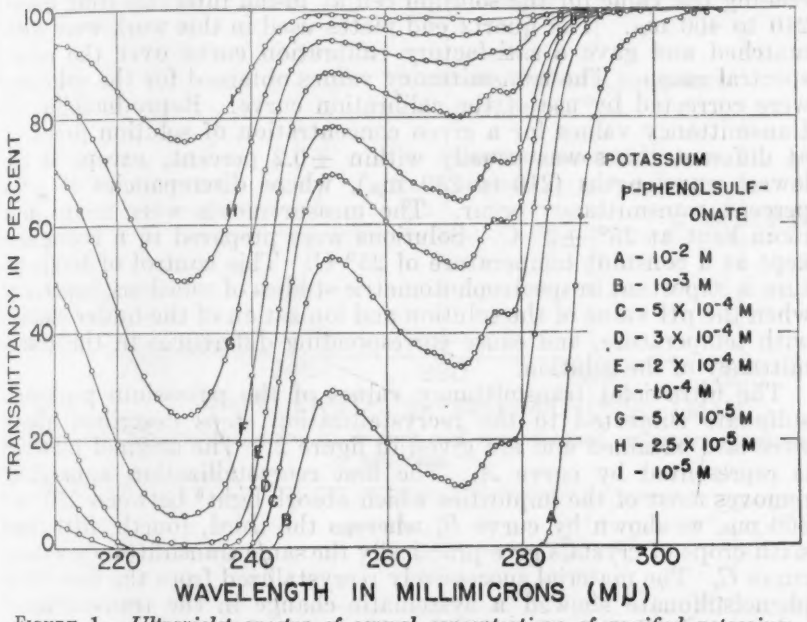

FIGURE 1.—*Ultraviolet spectra of several concentrations of purified potassium p-phenolsulfonate.*

tion index is determined by dividing the index ($-\log_{10}$ transmittancy) for that solution by the concentration multiplied by the depth of the solution (cell length in centimeters) through which the light beam passes, according to Beer's law. If the molar absorption indices do not agree well within experimental error for several wavelengths, then dissociation, association, or some chemical change is suspected. For this purpose the absorption indices of solutions of phenolsulfonate 10^{-4}, 2×10^{-4}, and 3×10^{-4} molar in water were first compared. Additional solutions of the same concentrations were made in 10^{-1} molar hydrochloric acid. These data agreed well within experimental error for practically the entire absorption curve, except on the steep portions of the bands where the errors are large, showing that the sulfonate group is completely ionized and the phenolic group non-ionized in all the above solutions. As an additional check, a 10^{-4} molar solution in the 5-cm cells was compared with a solution in the 1- and 2-cm cells. The agreement was well within experimental error.

The spectrophotometric data were obtained by use of a Beckman quartz photoelectric spectrophotometer.[4] It was improved by the

[4] Made by the National Technical Laboratories, Pasadena, Calif. Described in J. Opt. Soc. Am. 31, 682 (1941).

replacement of the cell compartment [5] by a small light-tight box with a slide for holding two 38-mm (i. d.) cylindrical metal cell holders in which Pyrex cylinders of 1-, 2-, and 5-cm lengths could be fitted with quartz end plates to hold the solutions. One cell was filled with the solution under investigation. The solvent, or 100-percent cell, contained the same components of the solution except the compound under investigation. The cells were placed alternately in the light beam for the transmittancy measurements. They were calibrated each day at the beginning and end of the test by filling both cells with distilled water, using the solvent cell for 100-percent transmission and reading the value for the solution cell at 10-mμ intervals from about 210 to 400 mμ. The quartz end plates used in this work were well-matched and gave a satisfactory calibration curve over the entire spectral range. The transmittancy values obtained for the solutions were corrected by use of the calibration curve. Reproducibility of transmittancy values for a given concentration of solution prepared at different times was usually within ± 0.2 percent, except at the lowest wavelengths (210 to 230 mμ), where discrepancies of ± 0.5 percent transmittancy occur. The measurements were made in a room kept at 25° ± 2° C. Solutions were prepared in a room also kept at a constant temperature of 25° C. This control of temperature is important in spectrophotometric studies of solutions, especially when the pH value of the solution and ionization of the buffer change with temperature, and cause corresponding differences in the transmittancy of the solution.

The ultraviolet transmittancy values of the potassium *p*-phenolsulfonate subjected to the recrystallization steps described above were also obtained and are given in figure 2. The original material is represented by curve *A*. The first recrystallization apparently removes most of the impurities which absorb light [6] between 250 and 300 mμ, as shown by curve *B*, whereas the third, fourth, fifth, and sixth crops of crystals give practically the same transmittancy values, curve *C*. The material successively recrystallized from the first lot of phenolsulfonate showed a systematic change in the transmittancy values, as in the bromine analyses (given in table 2 but not shown in fig. 2).

Studies of a number of buffers have shown them to be highly resonant and chromophoric in the ultraviolet, and also that their absorption index bands are altered greatly by pH changes, just as in the case of indicators in the visible, ultraviolet, and infrared regions. Some measurements therefore were made of the ultraviolet absorption of solutions of the secondary *p*-phenolsulfonate salt, which is formed when alkali is added to a solution of the primary salt. The spectrophotometric curves shown in figure 3 represent the *p*-phenolsulfonate, 5×10^{-5} molar, in 10^{-1} molar hydrochloric acid (curve *A*) and the same concentration in 10^{-3} molar sodium hydroxide (curve *D*). The two intermediate curves, *B* and *C*, were obtained by using dilute borax–boric-acid buffers of pH 8.4 and 9.0, which do not have absorption bands in this region. In these dilute solutions there may have been some error due to the absorption of carbon dioxide during the

[5] The authors are indebted to Jurg. A. Senn for help in designing the metal box, as well as other improvements in the electric circuit, and calibration of the instrument. Extensive data, which have not yet been reported, were obtained previously with filters and indicator solutions to test the performance of the instrument. The precision is about ± 0.5 on the scale from 0.0- to 100.0-percent transmittancy.

[6] For example, figure 3 shows that any secondary salt present as impurity absorbs strongly between 240 and 300 mμ.

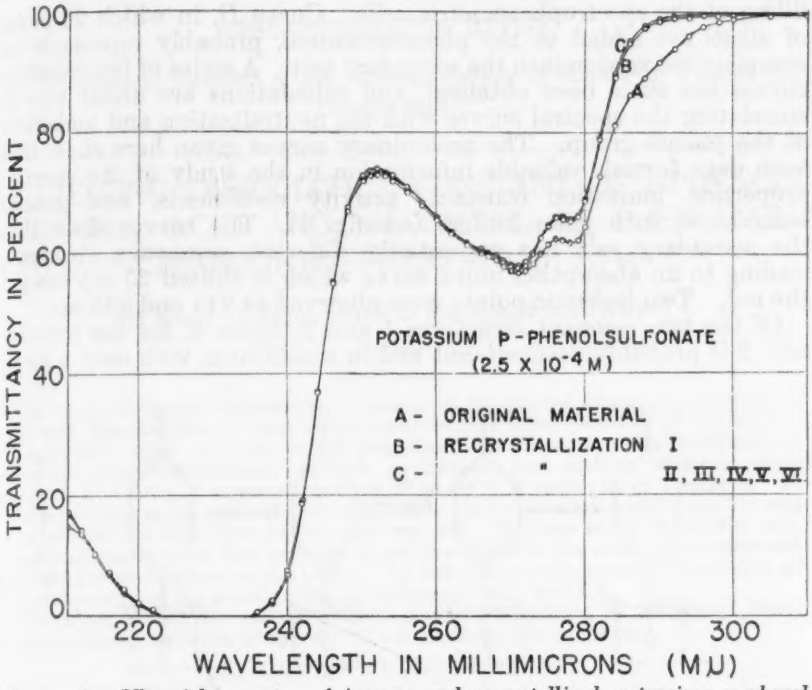
TRANSMITTANCY IN PERCENT
WAVELENGTH IN MILLIMICRONS (Mμ)
POTASSIUM P-PHENOLSULFONATE
(2.5 X 10⁻⁴ M)
A - ORIGINAL MATERIAL
B - RECRYSTALLIZATION I
C - " II, III, IV, V, VI

FIGURE 2.—*Ultraviolet spectra of impure and recrystallized potassium p-phenolsulfonate.*

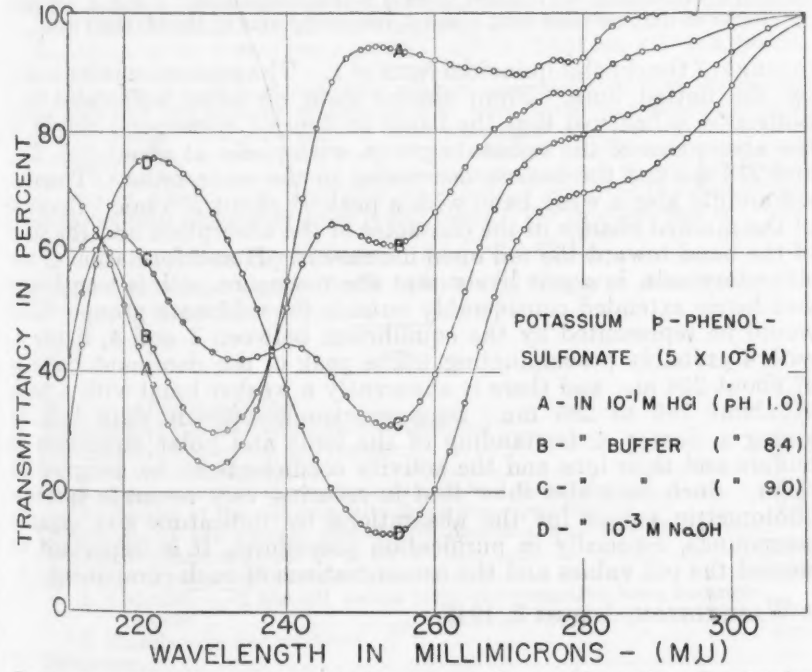
TRANSMITTANCY IN PERCENT
WAVELENGTH IN MILLIMICRONS - (Mμ)
POTASSIUM P-PHENOL-
SULFONATE (5 X 10⁻⁵ M)
A - IN 10⁻¹ M HCl (PH 1.0)
B - " BUFFER (" 8.4)
C - " " (" 9.0)
D - " 10⁻³ M NaOH

FIGURE 3.—*Ultraviolet spectra which represent the transformation of potassium p-phenolsulfonate from the primary to the secondary salt.*

filling of the spectrophotometric cells. Curve *D*, in which 20 moles of alkali are added to the phenolsulfonate, probably represents its complete conversion into the secondary salt. A series of intermediate curves has since been obtained, and calculations are under way in correlating the spectral curves with the neutralization and ionization of the phenol group. The preliminary curves given here show that such data furnish valuable information in the study of the spectral properties, ionization constant, activity coefficients, and general behavior of such polar buffers (see fig. 4). The curves show that the secondary salt has an entirely different resonance structure, leading to an absorption index curve which is shifted 25 mμ toward the red. Two isobestic points were observed at 215 and 238 mμ.

Of the two resonant structures 1 and 2, figure 4, for the primary salt, 2 is probably predominant and in equilibrium with only a small

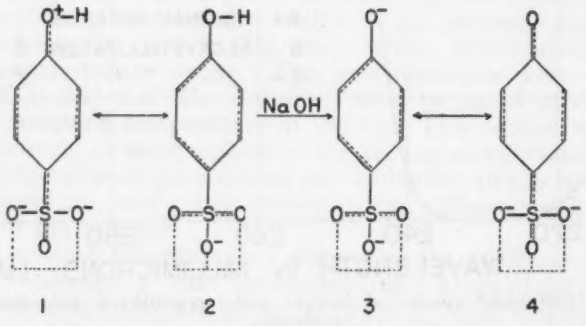

FIGURE 4.—*Structural and resonant forms of p-phenolsulfonates.* 1 and 2, resonant forms of the univalent salt; 3 and 4, resonant forms of the bivalent salt.

amount of the dipolar quinoidal form of 1. The resonance is indicated by the dotted lines. From similar data on other sulfonates and buffers, it is believed that the bands in figure 1 correspond chiefly to the absorption of the sulfonate group, with peaks at about 230, 271, and 278 mμ and the indices decreasing in the same order. There is apparently also a weak band with a peak at about 266 mμ. Because of the marked change in the character of the absorption and the shift of the band toward the red upon increase in pH and formation of the secondary salt, it seems likely that the resonance path is lengthened and hence extended considerably outside the sulfonate group. This would be represented by the equilibrium between 3 and 4, figure 4, with 4 probably predominating. The peak of the dominant band is at about 254 mμ, and there is apparently a weaker band with a peak at about 280 to 285 mμ. Such spectrophotometric data help in giving a clearer understanding of the ionic and polar structures of buffers and their ions and the activity coefficients to be assigned to them. Such data also show that in securing very accurate spectrophotometric values for the absorptions by indicators and organic compounds, especially in purification procedures, it is important to control the pH values and the concentrations of each component.

WASHINGTON, August 7, 1943.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1559

Part of Journal of Research of the National Bureau of Standards, Volume 31, October 1943

THE SECOND DISSOCIATION CONSTANT OF *p*-PHENOLSULFONIC ACID AND pH VALUES OF PHENOLSULFONATE-CHLORIDE BUFFERS FROM 0° TO 60° C.

By Roger G. Bates, Gerda L. Siegel, and S. F. Acree

ABSTRACT

The thermodynamic dissociation constant of the phenol group of *p*-phenolsulfonic acid was calculated from electromotive-force measurements of hydrogen-silver-chloride cells without liquid junction. Thirty-nine buffer mixtures of potassium *p*-phenolsulfonate, sodium hydroxide, and sodium chloride were studied in five series of experiments from 0° to 60° C at intervals of 5 degrees. In three series, the molal ratio of phenolsulfonate ion to phenolate-sulfonate ion was unity, and in two series the buffer ratio was 2:3. For two series of experiments, one at each buffer ratio, the molality of sodium chloride was maintained constant near 0.05 for all dilutions of the buffer. In the other experiments, the molality of each component of the solution varied between 0.0037 and 0.1.

The values of pK_2, the negative of the common logarithm of the second dissociation constant, between 0° and 60° C are given by the equation

$$pK_2 = 1961.2/T - 1.1436 + 0.012139T,$$

where T is in degrees Kelvin.

Equations were formulated to give the changes of free energy, heat content, entropy, and heat capacity that accompany the dissociation, at infinite dilution, of a mole of phenolsulfonate ion at any temperature between 0° and 60° C. For the dissociation of the phenol group at 25° C, $\Delta F°$ is 12,351 cal, $\Delta H°$ is 4,036 cal, $\Delta S°$ is -27.9 cal deg^{-1}, and $\Delta C°p$ is -33 cal deg^{-1}.

The pH value of each buffer-chloride mixture was calculated from the experimental data and the activity coefficients that were found to characterize each series of solutions. The pH values of other phenolsulfonate buffers which have molal ratios, m_1/m_2, of phenolsulfonate ion to bivalent phenolate-sulfonate ion between 2/3 and 1 can be computed for temperatures between 0° and 60° C with an accuracy of ± 0.002 unit from their compositions and from the dissociation constants and ionic parameters given in this paper. The equation used is

$$pH = pK_2 - \log(m_1/m_2) - 3A\sqrt{\mu}/(1 + 8B\sqrt{\mu}),$$

where μ is the ionic strength. Buffer solutions of this type are suitable pH standards in the range 8.6 to 9.0.

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I. ALKALINE BUFFER STANDARDS

Few acids are known whose dissociation constants fall in the region 10^{-7} to 10^{-9}. Consequently, few buffer standards with pH values between 7.0 and 9.0 are available for the calibration of pH equipment and for the control of acidity. Regulation of pH in this slightly alkaline region is, however, of great importance in studies of biological processes and of the body fluids, in the treatment of water, and in the processing of foods and medicines.

Among the buffer solutions that have been employed in this range are mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate, mixtures of boric acid and borax, and solutions of glycine and sodium hydroxide [1].[1] At a pH of 7.5, however, the second acid hydrogen of phosphoric acid is 85 percent neutralized [2]. The pH values of phosphate buffers above pH 7.5 are, therefore, considerably influenced by contamination of the solution with carbon dioxide and by accidental errors in composition. The same objection applies to the use of mixtures of glycine and sodium hydroxide below pH 9.

Borax solutions have pH values of about 9.2, and a buffer composed of borax and boric acid must contain considerable amounts of free boric acid if a pH of 8.2 is to be achieved. Furthermore, such solutions may contain appreciable concentrations of associated polyboric acids [3, 4]. Until boric acid solutions have been further investigated, their pH values between pH 8 and pH 9 will be subject to some uncertainty.

The substituted phenols are acids, and the acid strength varies widely with the number and kinds of substituents. In the search for a useful buffer standard for the slightly alkaline region, several phenols were found that had suitable dissociation constants. Many of these substances, like phenol itself, are liquids or low-melting solids. Some are hygroscopic, unstable to heat or to light, or otherwise unsuitable as standard materials.

The sodium and potassium hydroxybenzoates and hydroxybenzenesulfonates (phenolsulfonates), however, are typical salts and are free from most of these objections. They are crystalline materials, stable at 110° C, and may be recrystallized readily from water. Acree, Mellon, Avery, and Slagle [5] have suggested the use of phenolsulfonates in the preparation of solutions of known acidity. Furthermore, the pH values of buffer systems composed of bivalent and univalent anions can be determined with less difficulty than can those of buffers of a weak monobasic acid and its alkali-metal salt. A dibasic-acid buffer, a mixture of potassium phenolsulfonate and sodium hydroxide for example, covers a much larger range of pH on dilution than does a monobasic-acid system, without sacrifice of considerable buffer capacity.

An electrometric titration of sodium *p*-phenolsulfonate with sodium hydroxide solution showed that the phenol group of *p*-phenolsulfonic acid, one of the simplest dibasic acids of this type, was half neutralized at about pH 8.7. Further substitution of hydrogen in the benzene ring with halogen increases the dissociation of the phenol. Potassium *p*-phenolsulfonate is anhydrous at room temperature, and is therefore more satisfactory than the hydrated sodium salt for the preparation of standard buffers.

[1] Figures in brackets indicate the literature references at the end of this paper.

It is the purpose of this paper to report the measurement of the dissociation constant of the phenol group of *p*-phenolsulfonic acid at 5-degree intervals from 0° to 60° C. The pH values of certain mixtures of potassium *p*-phenolsulfonate, sodium hydroxide, and sodium chloride have been determined. These solutions are proposed as pH standards in the range 8.6 to 9.0.

II. DISCUSSION OF THE ELECTROMOTIVE-FORCE METHOD

The calculation of the second dissociation constant, K_2, of a weak acid and the pH values of solutions of the acid mixed with its salts from emf measurements of hydrogen–silver-chloride cells has been outlined in earlier publications from this Bureau [2, 6, 7]. Mention should be made, however, of the assumptions upon which these calculations are based.

In the absence of side reactions, a cell that contains hydrogen and silver–silver-chloride electrodes is reversible to hydrogen and chloride ions, and its potential depends upon the product of the activities of these ions alone. If the molalities, m, of these ions are known, the cell potential then gives the activity coefficient product, $f_{\mathrm{H}}f_{\mathrm{Cl}}$. The square root of this product, $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$, is the mean activity coefficient of hydrochloric acid, $f_{\pm}$. It is related to the partial molal free energy, or "chemical potential," of hydrochloric acid in the solution, and may be evaluated by several methods which include measurements of freezing point and vapor pressure as well as of emf.

The activity or activity coefficient of a single ion species cannot be evaluated by the methods of thermodynamics alone. Hence to obtain a pH value, or negative of the common logarithm of the activity of the hydrogen ion, an extra-thermodynamic assumption must be made to relate ionic activity to measurable quantities. The dissociation constant, however, is obtained by extrapolation of an appropriate function of emf to the limit at infinite dilution, where all of the activity coefficients are equal. Its value is free from assumptions which interrelate activity coefficients of the ions in the mixture.

For a starting point in the calculation of ionic activity coefficients from emf measurements of cells of the type used here, it is customary to consider that the activity coefficients of hydrogen and chloride ions in the mixture are equal to the mean activity coefficient of hydrochloric acid. This assumption was proposed by Guggenheim [8] and has been used widely. It is further assumed that all ions of the same numerical charge have identical activity coefficients. In this case, then,

$$f_i=\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}, \tag{1}$$

when i represents a singly charged ion.

It has been found that the measured stoichiometrical activity coefficients of many electrolytes in very dilute aqueous solution approach the theoretical values calculated from the Debye-Hückel limiting-law expressions for each of their component ions:

$$-\log f_i=Az_i^2\sqrt{\mu}, \tag{2}$$

where μ is the ionic strength and z_i is the valence of the ion i. The Hückel equation [9],

$$-\log f_i = \frac{Az_i^2\sqrt{\mu}}{1+Ba_i\sqrt{\mu}} - \beta\mu, \tag{3}$$

has been shown to represent the activity coefficient with considerable success at higher concentrations, as well. The constants A and B of eq 2 and 3 vary with temperature and dielectric constant. The symbols a_i and β represent adjustable parameters. The dimensions of a_i are cm$\times 10^{-8}$. The term $\beta\mu$ can be considered as the resultant of several effects which contribute to $-\log f_i$. These contributions, which vary linearly with ionic strength, undoubtedly include the change of dielectric constant with concentration of ionized solutes as well as interactions among resonant dipolar ions and nonpolar ions.

For the calculation of pH values, therefore, the mean activity coefficients of hydrochloric acid in the mixtures are represented by eq 3 (with $z_i^2=2$), and the activity coefficients of all ions in the mixture are expressed in terms of $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$. The activity coefficients of all univalent ions are set equal to $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$ (eq 1). The relationship between the activity coefficients of univalent and bivalent ions is given by eq 3. The activity coefficient of a bivalent anion, $A^=$, in the mixture is then given in terms of the mean activity coefficient of hydrochloric acid by

$$-\log f_{A^=} = -4\log\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}} + 3\beta\mu. \tag{4}$$

The same values of a_i and β are assumed to apply to all ions of a particular mixture at a particular temperature. The values of these parameters are considered to be weighted averages for all the types of ions in the solution.

Although the value of pK_2 is independent of the validity of any expression for activity coefficients, the extrapolation to zero ionic strength is considerably facilitated when a fairly close approximation to each activity coefficient can be made. When eq 2 is combined with the fundamental emf equation for the hydrogen–silver-chloride cell and with the equilibrium expression for the second step in the dissociation of *p*-phenolsulfonic acid,

$$\underset{\text{(phenolsulfonate)}}{HOC_6H_4SO_3^-} = H^+ + \underset{\text{(phenolate-sulfonate)}}{C_6H_4(SO_3^-)(O^-)}, \tag{5}$$

the following equation[2] is obtained:

$$pK_2' = (E-E^\circ)/k + \log(m_{\mathrm{HPs}}m_{\mathrm{Cl}}/m_{\mathrm{Ps}}) + 2A\sqrt{\mu}, \tag{6}$$

where pK_2' is the negative logarithm of the "apparent dissociation constant." Upon extrapolation to infinite dilution. pK_2' becomes pK_2. The symbols E and E° represent, respectively, the emf and standard potential of the cell, and k is $2.3026RT/F$. The gas constant, R, has the value 8.3127 int. j deg^{-1} mole^{-1} [10]; T is the absolute temperature ($t+273.16$, where t is in degrees centigrade [11]; and F is the

[2] In this equation, and elsewhere in this paper, Ps represents the phenolsulfonate ion and Ps represents the phenolate-sulfonate ion.

faraday (9.650×10^4 int. coulombs [11]). The standard potential, $E°$, has been measured at 5-degree intervals from 0° to 60° C by Harned and Ehlers [12]. Its value was recalculated by Hamer, Burton, and Acree [6], and is listed in their paper, together with the constants A and B of eq 2 and 3. The values of k in international units are also given in an earlier publication from this Bureau [2].

When eq 3 is used for each activity coefficient, the dissociation constant is represented by an equation similar to eq 6 in form:

$$pK_2'=pK_2-\beta\mu=(E-E°)/k+\log(m_{HPs}m_{Cl}/m_{Ps})+2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}). \quad (7)$$

It is usually possible to choose a value of a_i that will make pK_2' a linear function of μ. The slope of the plot of pK_2' with respect to μ is $-\beta$, and the intercept at zero ionic strength is pK_2, the thermodynamic dissociation constant.

In this way the values of a_i and β that fit a particular series of mixtures are established. When these values of the parameters are employed, eq 3 (with $z_i^2=1$) represents the negative of the logarithm of the mean activity coefficient of hydrochloric acid, $-\log\sqrt{f_H f_{Cl}}$. Equation 3 also represents, as we have assumed, the negative logarithm of the activity coefficient of each ion species in the mixture, when the appropriate value of z_i is used. It is then a simple matter to compute pH values from eq 8 for the emf of the cell, with the substitution of the right side of eq 3 for $-\log f_{Cl}$ [13]:

$$pH=(E-E°)/k+\log m_{Cl}-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta\mu. \quad (8)$$

In the use of eq 6 and 7 it should be realized that hydrolysis of some of the phenolate-sulfonate ion lowers the molality of that ion and increases the molality of phenolsulfonate ion by the same margin. It was found that at 25° C not more than 0.3 percent of the phenolate-sulfonate ion in any of the buffers used in this investigation was hydrolyzed. If the effect of this hydrolysis had not been considered in the calculations, however, a maximum error of 0.01 unit would have been included in the pK_2' values for the most dilute buffer at the highest temperature measured. Hydrolysis affects the calculation of pH by eq 8 only through changes in a_i, β, and μ. At room temperature these errors are negligible. At higher temperatures, however, hydrolysis is considerably enhanced. Corrections for hydrolysis therefore were made at each temperature.

If m_1 is the stoichiometrical molality of phenolsulfonate salt, m_2 that of the phenolate-sulfonate, and m_3 that of sodium chloride, the ratio m_{HPs}/m_{Ps} is given by

$$m_{HPs}/m_{Ps}=(m_1+m_{OH})/(m_2-m_{OH}). \quad (9)$$

When m_{OH} is known, the ionic strength may also be calculated:

$$\mu=m_1+3m_2+m_3-m_{OH}. \quad (10)$$

The molality of hydroxyl ion, m_{OH}, can be computed directly from the emf data by the equation

$$(E-E°)/k=pK_w+\log(m_{OH}/m_{Cl})+\log(f_{OH}/f_{Cl}), \quad (11)$$

or

$$-\log m_{OH}=pK_W-(E-E°)/k-\log m_{Cl}, \quad (11a)$$

where pK_w is the negative of the common logarithm of the thermodynamic dissociation constant (ion product) of water at the stated temperature [14]. Equations 11 and 11a were derived by the substitution of the equilibrium expression for the dissociation of water into the equation that relates the emf of the hydrogen–silver-chloride cell to the activities of hydrogen and chloride ions. The last term of eq 11 is zero, as a result of the assumed equality of the activity coefficients of the two univalent ions. The computation of hydrolysis corrections is accordingly a simple matter.

III. EXPERIMENTAL PROCEDURE AND RESULTS

1. MATERIALS

A commercial preparation of potassium *p*-phenolsulfonate was recrystallized four times from water at temperatures below the boiling point of the saturated solution. Only the first crops of crystals were retained. A slightly pink color observed when the commercial material was dissolved in water was discharged by the use of an activated vegetable carbon furnished by the Polarimetry Section of this Bureau. The mother liquors from subsequent recrystallizations were colorless. Tests showed the presence of sulfate in the original material, but this impurity was removed by the first recrystallization.

The potassium *p*-phenolsulfonate was assayed by measurement of the amount of bromine consumed under conditions such that two atoms of bromine were readily substituted and further substitution was negligible.[3] The sample (0.001 mole of the salt in 200 ml of 1 *M* hydrochloric acid) was brought to a temperature of 0° to 0.4° C and allowed to react with bromine (formed by the addition of a slight excess of a standard solution of potassium bromate and potassium bromide) for 15 minutes. The excess bromine was then determined by the addition of potassium iodide and titration of the iodine with thiosulfate solution. Potassium bromate was used as a primary standard, and the thiosulfate solution was compared frequently with the bromate-bromide solution by means of blank analyses from which the potassium phenolsulfonate was omitted.

Three bromometric analyses gave 100.03 $\pm$0.1 percent for the purity of the first preparation (employed for solutions A1 to A9). The second preparation, from which the remaining buffer solutions were prepared, gave 100.09 $\pm$0.1 percent for the mean of three analyses. Three differential electrometric titrations of the first sample gave a mean of 100.08 percent, with an average departure from the mean of 0.2 percent. The blank correction was determined with Nile Blue A sulfate.[4] The electrometric end point was readily estimated to within 0.2 percent by graphical means, but a further uncertainty of nearly the same magnitude was introduced with the use of a blank correction. The results of the titrations of the phenol group with alkali must, therefore, be considered as only corroborative evidence of the purity of the salt. An error of 0.1 percent in the purity of the potassium phenolsulfonate introduces an error of 0.0009 unit in pK_2.

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[3] This method of analysis was adapted by E. E. Sager, of this Bureau, from the experimental conditions for the bromometric determination of furfural [15]. The authors are indebted to Mrs. Sager for the purification and analysis by this method of the sample of potassium phenolsulfonate from which buffer solutions A1 to A9 were prepared.

[4] The color range of this indicator (10.3 to 12.0) includes the pH at which the neutralization of the phenol is complete. The pH-titration curve of *p*-phenolsulfonic acid, determined electrometrically, indicates that a 0.04-*M* solution of disodium phenolate sulfonate has a pH of about 10.7.

The first preparation of phenolsulfonate was analyzed by the Metal and Ore Analysis Section of this Bureau with the following results: carbon—34.02, 34.03 percent; hydrogen—2.40, 2.57 percent; sulfur—14.98 percent. The theoretical percentages of these elements are, respectively, 33.95, 2.37, and 15.10.

Anhydrous potassium *p*-phenolsulfonate is the form of the salt stable at room temperature. When exposed to laboratory air of about 20- to 30-percent humidity, a dry sample absorbed 0.03 to 0.05 percent of moisture. This water was readily lost at 110° C, and the salt was always dried at this temperature before the buffer solutions were prepared. The use of temperatures higher than 110° C should be avoided. One sample was heated overnight at 170° C, and was found thereafter to give a positive test for sulfate. When the salt is heated in air at temperatures of 150° C and above, the odor of phenol is apparent.

Sodium chloride was precipitated from its saturated aqueous solution with dry hydrogen chloride. The salt was then fused in platinum to remove occluded acid. It was fractured and bottled without grinding.

A solution of sodium hydroxide was prepared by dilution of a 50-percent alkali solution that had been centrifuged to remove the insoluble sodium carbonate. The diluted solution was kept in a bottle lined with paraffin and was protected from the air by a guard tube of soda-lime. The solution was standardized frequently against acid potassium phthalate. The average deviation of the analyses was about 0.03 percent.

2. PREPARATION OF THE BUFFER SOLUTIONS AND ELECTRODES

All the solutions were prepared by weight methods. For each series of experiments, a stock solution was prepared from weighed amounts of sodium chloride, potassium *p*-phenolsulfonate, and sodium hydroxide solution. Ten dilutions of this stock solution were made in the manner described earlier by Bates and Acree [2]. The specific conductance of the water was usually less than 0.6×10^{-6} mho. For two series of experiments, the dilutions were made with a sodium chloride solution that had the same molality of salt as the stock solution. It was found that the cells attained equilibrium somewhat more rapidly when the solutions were saturated with hydrogen instead of with nitrogen. In the preparation of the phenolsulfonate buffers, carbon-dioxide-free air was passed through each solution flask while the dilution was being made. The solutions were then freed of air by passing hydrogen through them for about 2 hours before the final weighings were made. The weights were corrected to a vacuum basis.

The hydrogen electrodes were prepared by a modification of the method of Popoff, Kunz, and Snow [16]. The platinum foils were plated lightly with gold and then electrolyzed for 90 seconds in a 3-percent solution of chloroplatinic acid. The electrodes were cleaned by electrolysis in concentrated hydrochloric acid solution. The silver–silver-chloride electrodes were considerably smaller than those described by Hamer and Acree [13] but were larger than the "semimicro" type used by Bates, Siegel, and Acree [17] for electrometric titrations in a cell without liquid junction. About 65 mg of silver was formed by heating a paste of silver oxide at 540° C on a spiral of platinum

3 mm in diameter and 5 mm long. Approximately 20 percent of the silver was converted to silver chloride by electrolysis in 1-*M* hydrochloric acid solution for 45 minutes with a current of 5 ma.

Hydrogen and silver chloride electrodes were always freshly prepared for each series of experiments. The cells contained two electrodes of each kind. The silver chloride electrodes were checked for agreement in a 0.05-*m* solution of hydrochloric acid, and only those electrodes that agreed in potential within 0.06 mv were used. The "aging effect" of silver chloride electrodes, or change of potential during the first few hours after preparation, has been shown by Smith and Taylor [18] to result from the slow diffusion of electrolyte into the pores of the electrode. Thick, adherent layers of silver chloride retard the diffusion and prolong the period of aging. To obviate errors due to concentration-polarization, all the cells were prepared at least 18 hours before measurements were made.

3. RESULTS OF THE ELECTROMOTIVE-FORCE MEASUREMENTS

The cells were usually filled in the late afternoon, kept at 25° C overnight, and measured throughout the following day before the temperature of the water bath was lowered for the measurements at temperatures below 25° C on the third day. The measurements in the range 25° to 60° C were made on the fourth day, and the temperature brought back to 25° C for a final check. The zero point of the thermometer was usually redetermined before each series of experiments was begun. Other experimental details are given in an earlier publication [2].

The electromotive forces, corrected to a hydrogen partial pressure of 760 mm, are given in tables 1 and 2, together with the molalities of potassium *p*-phenolsulfonate (m_1), potassium sodium *p*-phenolate sulfonate (m_2), and sodium chloride (m_3) in each of the buffer solutions. The accuracy of the emf values is probably about ± 0.1 mv (± 0.0017 pH unit). It may be seen that the "buffer ratio", m_1/m_2, is approximately unity for solutions of series A and series C, whereas the solutions of series B and D have a buffer ratio of about 2:3. In all the buffers that make up series C and D, the chloride molality (m_3) was kept constant near 0.05. This device was advantageous in assuring reproducibility and rapid attainment of equilibrium of the silver chloride electrodes at low concentrations of the buffer salts.

TABLE 1.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate (m_1), potassium sodium p-phenolate sulfonate (m_2), and sodium chloride (m_3): series A and B*

Solution number	m_1	m_2	m_3	$E_{0°}$	$E_{5°}$	$E_{10°}$	$E_{15°}$	$E_{20°}$
A1	0.09628	0.09744	0.09622	0.78744	0.79105	0.79460	0.79807	0.80156
A2	.05979	.06051	.05975	.79000	.80295	.80674	.81048	.81418
A3	.04130	.04180	.04127	.80826	.81235	.81636	.82030	.82419
A4	.03070	.03107	.03068	.81578	.82003	.82419	.82830	.83235
A5	.016220	.016416	.016210	.83202	.83667	.84118	.84567	.85004
A6	.009425	.009539	.009419	.84605	.85091	.85570	.86040	.86502
A7	.007710	.007803	.007705	.85125	.85633	.86118	.86604	.87077
A8	.005805	.005875	.005801	.85848	.86355	.86858	.87349	.87830
A9	.003703	.003748	.003701	.86994	.87525	.88048	.88565	.89073
A10	.09780	.09873	09761	.78720	.79081	.79425	.79766	.80100
A11	.06503	.06565	.06491	.79700	.80094	.80464	.80828	.81190
A12	.05321	.05371	.05311	.80197	.80595	.80975	.81351	.81731
A13	.03944	.03982	.03937	.80949	.81361	.81762	.82152	.82540
A14	.017758	.017927	.017724	.82977	.83433	.83874	.84308	.84744
A15	.016094	.016248	.016063	.83223	.83683	.84128	.84569	.85007
A16	.008621	.008703	.008604	.84818	.85308	.85785	.86256	.87525
A17	.003723	.003758	.003716	.86964	.87496	.88016	.88529	.89043

TABLE 1.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate (m_1), potassium sodium p-phenolate sulfonate (m_2), and sodium chloride (m_3): series A and B*—Continued

Solution number	m_1	m_2	m_3	$E_{0°}$	$E_{5°}$	$E_{10°}$	$E_{15°}$	$E_{20°}$
B1	.07306	.09859	.10110	.79311	.79682	.80051	.80410	.80763
B2	.04951	.06682	.06851	.80264	.80642	.81030	.81413	.81784
B3	.04269	.05761	.05907	.80624	.81010	.81409	.81798	.82178
B4	.02465	.03326	.03411	.81995	.82425	.82847	.83265	.83676
B5	.012009	.016207	.016618					
B6	.010339	.013953	.014307	.84216	.84694	.85162	.85621	.86075
B7	.006241	.008422	.008636	.85533	.86034	.86528	.87015	.87496
	$E_{25°}$	$E_{30°}$	$E_{35°}$	$E_{40°}$	$E_{45°}$	$E_{50°}$	$E_{55°}$	$E_{60°}$
A1	0.80500	0.80839	0.81169	0.81506	0.81838	0.82159	0.82482	0.82808
A2	.81793	.82157	.82517	.82878	.83229	.83583	.83930	.84278
A3	.82815	.83197	.83577	.83956	.84329	.84703	.85072	.85435
A4	.83644	.84046	.84441	.84839	.85224	.85613	.85993	.86376
A5	.85445	.85875	.86304	.86730	.87149	.87570	.87983	.88394
A6	.86979	.87434	.87888	.88343	.88789	.89234	.89664	.90104
A7	.87553	.88039	.88501	.88968	.89423	.89879	.90334	.90779
A8	.88332	.88813	.89294	.89771	.90246	.90715	.91152	.91617
A9	.89589	.90099	.90597	.91092	.91577	.92060	.92534	.93002
A10	.80467	.80807	.81137	.81461	.81794	.82118	.82435	.82760
A11	.81565	.81928	.82284	.82641	.82989	.83335	.83681	.84024
A12	.82109	.82485	.82852	.83219	.83578	.83937	.84292	.84651
A13	.82942	.83332	.83716	.84101	.84476	.84851	.85220	.85590
A14	.85184	.85611	.86036	.86461	.86876	.87290	.87697	.88105
A15	.85450	.85886	.86313	.86742	.87160	.87576	.87994	.88410
A16	.87212	.87657	.88114	.88571	.89022	.89469	.89909	.90363
A17	.89555	.90054	.90559	.91051	.91541	.92016	.92488	.92953
B1	.81120	.81462	.81811	.82153	.82491	.82830	.83163	.83498
B2	.82172	.82541	.82910	.83272	.83633	.83993	.84349	.84706
B3	.82579	.82963	.83335	.83702	.84068	.84438	.84801	.85165
B4	.84097	.84504	.84902	.85301	.85697	.86093	.86474	.86863
B5	.86120							
B6	.86545							
B7	.87982	.88470	.88942	.89386	.89845	.90310	.90759	.91205

TABLE 2.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate (m_1), potassium sodium p-phenolate sulfonate (m_2), and sodium chloride (m_3): series C and D*

Solution number	m_1	m_2	m_3	$E_{0°}$	$E_{5°}$	$E_{10°}$	$E_{15°}$	$E_{20°}$
C1	0.10283	0.09862	0.04977	0.80179	0.80573	0.80932	0.81277	0.81674
C2	.08011	.07636	.05003	.80191	.80579	.80951	.81318	.81698
C3	.06418	.06118	.05003	.80212	.80603	.80987	.81360	.81731
C4	.05087	.04849	.05003	.80223	.80617	.81003	.81382	.81757
C5	.03578	.03411	.05003	.80243	.80657	.81047	.81428	.81806
C6	.015343	.014625	.05003	.80331	.80733	.81124	.81508	.81884
C7	.009787	.009329	.05003	.80392	.80797	.81194	.81583	.81967
D1	.06582	.09822	.04822	.81342	.81752	.82151	.82544	.82936
D2	.04586	.06834	.04824	.81353	.81761	.82166	.82566	.82964
D3	.03314	.04945	.04824	.81384	.81800	.82208	.82609	.83006
D4	.02682	.04002	.04825	.81404	.81823	.82235	.82638	.83034
D5	.02193	.03272	.04826	.81423	.81849	.82263	.82663	.83060
D6	.012187	.018186	.04826	.81471	.81899	.82312	.82715	.83117
D7	.006540	.009760	.04827	.81542	.81967	.82383	.82793	.83198
D8	.006003	.008958	.04827	.81543	.81961	.82378	.82788	.83189
	$E_{25°}$	$E_{30°}$	$E_{35°}$	$E_{40°}$	$E_{45°}$	$E_{50°}$	$E_{55°}$	$E_{60°}$
C1	0.82040	0.82401	0.82769	0.83130	0.83489	0.83846	0.84198	0.84549
C2	.82075	.82435	.82800	.83161	.83518	.83876	.84229	.84583
C3	.82108	.82472	.82836	.83201	.83563	.83923	.84269	.84629
C4	.82132	.82501	.82867	.83234	.83598	.83962	.84313	.84673
C5	.82185	.82560	.82930	.83297	.83663	.84024	.84382	.84743
C6	.82274	.82646	.83023	.83395	.83767	.84130	.84491	.84852
C7	.82353	.82731	.83105	.83468	.83835	.84201	.84560	.84913
D1	.83331	.83718	.84097	.84484	.84859	.85235	.85611	.85981
D2	.83364	.83750	.84136	.84526	.84905	.85284	.85661	.86033
D3	.83407	.83797	.84185	.84577	.84958	.85339	.85718	.86088
D4	.83437	.83830	.84220	.84613	.84996	.85378	.85758	.86136
D5	.83465	.83860	.84252	.84644	.85022	.85407	.85790	.86169
D6	.83529	.83917	.84310	.84705	.85090	.85470	.85851	.86228
D7	.83606	.84003	.84398	.84795	.85180	.85563	.85946	.86319
D8	.83601							

IV. CALCULATION OF THE SECOND DISSOCIATION CONSTANT AND RELATED THERMODYNAMIC QUANTITIES FROM 0° TO 60° C

In the search for the proper extrapolation function, the negative logarithm of the apparent dissociation constant, pK'_2, was computed for solutions A1 to A9 from eq 6, which comprises the Debye-Hückel limiting law. Examination of curve *A* of figure 1 shows that it would be difficult to obtain an accurate pK_2 value by extrapolation to infinite dilution with the use of eq 6. Equation 7 gave values of pK'_2 which, plotted as a function of ionic strength, lend themselves to an easy extrapolation. Curves *B*, *C*, and *D*, figure 1, were computed from eq 7 with a_i values of 4, 8, and 10 angstrom units, respectively. Corrections for hydrolysis by eq 9, 10, and 11a were made in all cases.

The use of 8 A was found to yield a straight line for the 4 series of buffers at each of the 13 temperatures. The error in establishing a_i is estimated to be less than ± 0.2 A. The slopes of these lines (β in eq 7) decreased with increasing temperature. The extrapolations of series A and B solutions followed a common course, in spite of the different buffer ratios involved. The β slopes for the two series (C and D), in which constant chloride molality was maintained, differed from each other, but β for series C was identical with the common slope of series A and B at all temperatures except 0° and 5° C.

TABLE 3.—*Numerical values of 3A, 8B, and β from 0° to 60° C*

t	$3A$	$8B$	$-\beta$		
			Series A and B	Series C	Series D
°C					
0	1.467	2.602	0.082	0.089	0.100
5	1.478	2.609	.075	.083	.093
10	1.490	2.616	.070	.070	.083
15	1.503	2.623	.066	.066	.081
20	1.516	2.631	.060	.060	.073
25	1.529	2.638	.057	.057	.069
30	1.544	2.647	.051	.051	.061
35	1.559	2.656	.049	.049	.060
40	1.575	2.664	.044	.044	.054
45	1.591	2.674	.041	.041	.053
50	1.607	2.682	.039	.039	.050
55	1.625	2.693	.041	.041	.055
60	1.643	2.702	.038	.038	.052

The values of β for all four series of solutions at the 13 temperatures are given in table 3, together with the values of $3A$ and $8B$. With the use of these constants and parameters, pK_2, the thermodynamic dissociation constant of the phenol group, was computed from eq 7. The mean value of pK_2 for each group of solutions is given in table 4. The seventh column of the table lists the average value for the five groups, weighted equally. Values of the dissociation constant, K_2, and of K_W/K_2 are given in the last two columns. The use of K_W/K_2 for approximate hydrolysis corrections will be described later. The uncertainty ascribed to pK_2 represents the mean departure of all 39 measurements from the average value. All the values at 0°, 25°, and 60° C are shown in figure 2, and the average pK_2 values are plotted as a junction of temperature in figure 3.

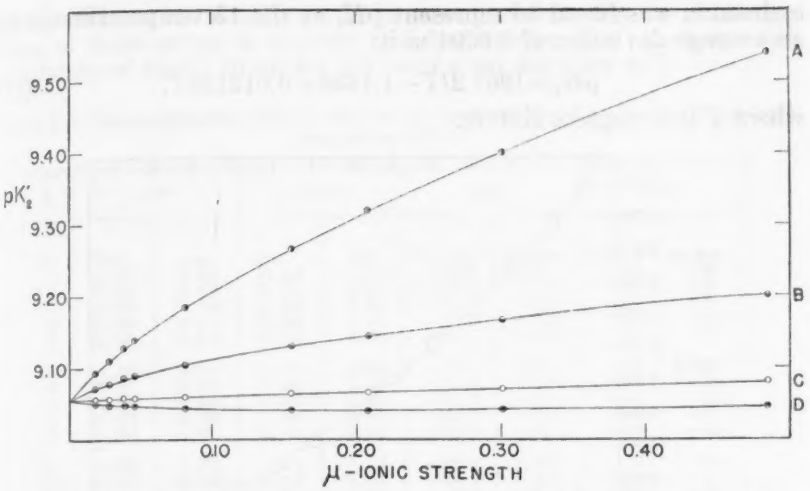

FIGURE 1.—*Extrapolation of the electromotive force data solutions A1 to A9.*

Curve *A* is calculated from eq 6; curves *B*, *C*, and *D* were computed from eq 7 with a_1 values of 4*A*, 8*A*, and 10*A*, respectively.

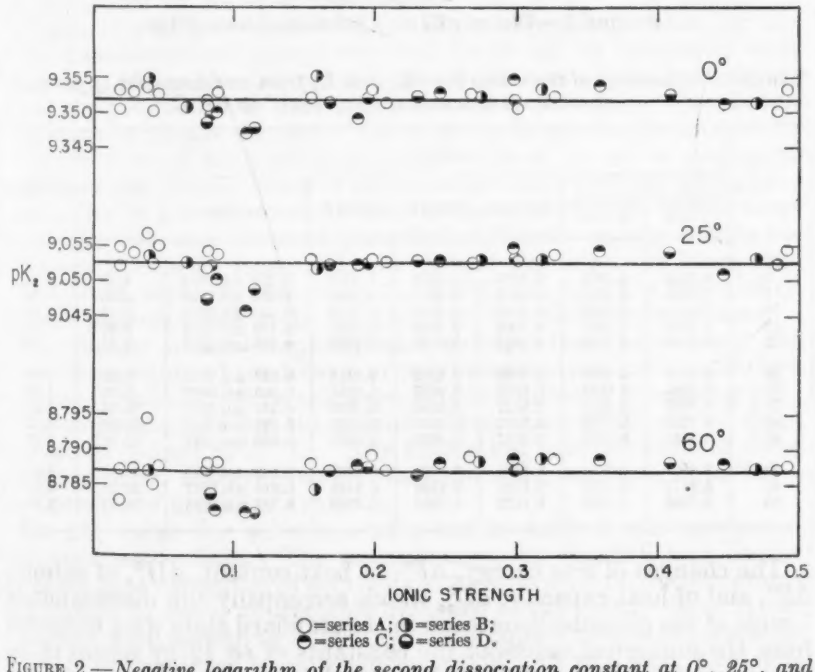

FIGURE 2.—*Negative logarithm of the second dissociation constant at 0°, 25°, and 60° plotted against ionic strength.*

The average values of pK_2 were fitted to the equation of Harned and Robinson [19] by the method of least squares. The following

expression was found to represent pK_2 at the 13 temperatures, with an average deviation of 0.0004 unit:

$$pK_2 = 1961.2/T - 1.1436 + 0.012139T, \quad (12)$$

where T is in degrees Kelvin.

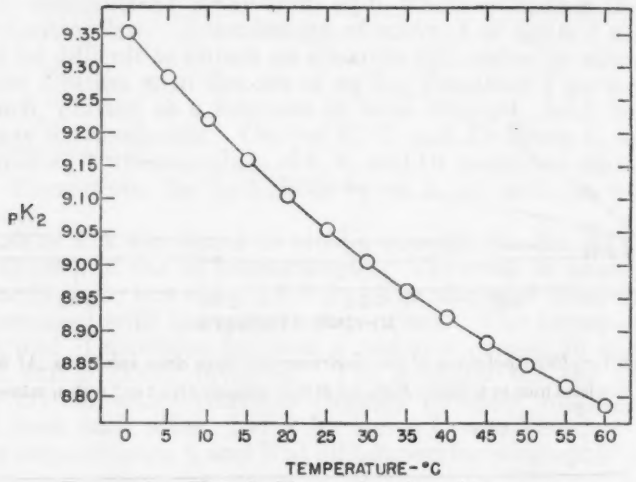

FIGURE 3.—*Plot of pK_2 as a function of temperature.*

TABLE 4.—*Summary of the values for pK_2 and K_2 from measurements of five groups of solutions at temperatures from 0° to 60° C*

t	pK_2						$K_2 \times 10^{10}$	$K_w/K_2 \times 10^4$
	Series A, 1 to 9	Series A, 10 to 17	Series B	Series C	Series D	Average		
°C								
0	9.3519	9.3521	9.3530	9.3513	9.3508	9.352 ±0.0014	4.45	0.258
5	9.2849	9.2846	9.2836	9.2837	9.2829	9.284 ±0.0014	5.20	.358
10	9.2210	9.2202	9.2198	9.2205	9.2195	9.220 ±0.0015	6.03	.485
15	9.1621	9.1603	9.1608	9.1594	9.1591	9.160 ±0.0015	6.92	.652
20	9.1064	9.1054	9.1048	9.1046	9.1038	9.105 ±0.0015	7.85	.868
25	9.0540	9.0530	9.0528	9.0516	9.0514	9.053 ±0.0013	8.85	1.138
30	9.0062	9.0054	9.0063	9.0035	9.0044	9.005 ±0.0017	9.89	1.489
35	8.9627	8.9613	8.9622	8.9596	8.9600	8.961 ±0.0017	10.94	1.910
40	8.9225	8.9212	8.9207	8.9191	8.9205	8.921 ±0.0017	12.00	2.43
45	8.8847	8.8837	8.8832	8.8825	8.8822	8.883 ±0.0017	13.09	3.07
50	8.8507	8.8491	8.8494	8.8481	8.8482	8.849 ±0.0018	14.16	3.87
55	8.8172	8.8158	8.8158	8.8146	8.8148	8.816 ±0.0017	15.28	4.77
60	8.7883	8.7872	8.7872	8.7863	8.7859	8.787 ±0.0018	16.33	5.89

The changes of free energy, $\Delta F°$, of heat content, $\Delta H°$, of entropy, $\Delta S°$, and of heat capacity, $\Delta C_p°$, which accompany the dissociation of 1 mole of the phenolsulfonate ion in the standard state were computed from the numerical values of the constants of eq 12 by means of the equations given in the paper of Bates and Acree [2]. These quantities are listed in table 5. For convenience, they are given both in calories and in international joules. One calorie has been taken as 4.1833 international joules [20].

The pK_2 values are thought to be correct within ±0.002 unit. The uncertainty in $\Delta F°$ introduced by the uncertainties in pK_2 is about

± 3 cal. The value of $\Delta S°$ may be in error by 0.3 cal deg^{-1}. A combination of these errors in entropy and free energy gives an estimated uncertainty of about 70 cal for $\Delta H°$ and 4 cal deg^{-1} for $\Delta C_p°$.

TABLE 5.—*Thermodynamic data for the second dissociation of p-phenolsulfonic acid from 0° to 60° C*

t	$\Delta F°$		$\Delta H°$		$\Delta S°$		$\Delta C_p°$	
°C	*int. j*	*cal*	*int. j*	*cal*	*int. j deg*$^{-1}$	*cal deg*$^{-1}$	*int. j deg*$^{-1}$	*cal deg*$^{-1}$
0	48,896	11,688	20,202	4,829	−105.0	−25.1	−127	−30
5	49,428	11,815	19,561	4,676	−107.4	−25.7	−129	−31
10	49,970	11,945	18,909	4,520	−109.7	−26.2	−132	−31
15	50,525	12,078	18,245	4,361	−112.0	−26.8	−134	−32
20	51,091	12,213	17,570	4,200	−114.4	−27.3	−136	−33
25	51,668	12,351	16,883	4,036	−116.7	−27.9	−139	−33
30	52,257	12,492	16,185	3,869	−119.0	−28.4	−141	−34
35	52,858	12,635	15,474	3,699	−121.3	−29.0	−143	−34
40	53,471	12,782	14,752	3,526	−123.7	−29.6	−146	−35
45	54,094	12,931	14,019	3,351	−126.0	−30.1	−148	−35
50	54.730	13,083	13,274	3,173	−128.3	−30.7	−150	−36
55	55,377	13,238	12,517	2,992	−130.6	−31.2	−152	−36
60	56,036	13.395	11,749	2,809	−132.9	−31.8	−155	−37

Unfortunately, there has been no direct calorimetric determination of the heat of dissociation of phenolsulfonate ion for comparison with that calculated by differentiation of the emf data. The change in heat capacity, $\Delta C_p°$, is smaller than the corresponding value for the second dissociation of phosphoric acid (−33 cal as compared with −54 cal). $\Delta C_p°$ is the difference between the sum of the heat capacities of the products and that of the reactants when the dissociation takes place at infinite dilution. Since the hydrogen ion is common to the dissociation of both acids, this difference of 21 cal in $\Delta C_p°$ must mean that the specific heats of the univalent and bivalent phosphate anions differ by a larger amount than do the specific heats of univalent phenolsulfonate and bivalent phenolate-sulfonate anions. This requirement is entirely reasonable, in view of the relatively large concentration of negative charge on the $HPO_4^=$ ion and the probability that the phenolate-sulfonate ion exists in two electromeric forms.

The changes in heat capacity and entropy that accompany the second dissociation of six dibasic or polybasic acids at infinite dilution are given in table 6. The acids are listed in order of increasing pK_2. The entropy changes for the second dissociation of all six of these acids are 30 ± 5 cal at 25° C. Any theoretical interpretation of these quantities must, however, await the time when accurate data for a large number of acids are available.

The $\Delta C_p°$ value for sulfuric acid given in table 6 was computed from calorimetric data. The measurements by Randall and Taylor [23] of the heat capacities of solutions of sulfuric acid at concentrations high enough to avoid appreciable influence of the second dissociation of the acid were plotted as a function of the square root of the molality and were extrapolated to zero concentration. In this way, 6 cal was found for the sum of the heat capacities of hydrogen and bisulfate ions at infinite dilution. Combination of this value with the heat capacities at infinite dilution of potassium sulfate [24] and of hydrochloric acid and potassium chloride [25] gave $\Delta C_p°$ for the second dissociation of sulfuric acid.

TABLE 6.—*Entropy and heat-capacity changes for the second dissociation of certain acids at 25° C*

Acid	$\Delta S°$ cal deg $^{-1}$	$\Delta C_p°$ cal deg $^{-1}$	Reference
Sulfuric	−26.3	[a] −73	Pitzer [21].[d]
Oxalic	[b] −24.8	−59	Harned and Fallon [22].
Malonic	−30.0	−61	Hamer, Burton, and Acree [6].
Phosphoric	[c] −29.6	[c] −45	Bates and Acree [2].
p-Phenolsulfonic	−27.9	−33	Bates, Siegel, and Acree.
Carbonic	−35.2		Pitzer [21].[d]

[a] Calculated by the authors from the data on the heat capacities of sulfuric acid solutions given by Randall and Taylor [23], together with the heat capacities at infinite solution of potassium sulfate (Randall and Rossini [24]) and of hydrochloric acid and potassium chloride (Rossini [25]).

[b] Calculated by the authors from the data of Harned and Fallon [22].

[c] The values of Nims [26], recalculated by Bates and Acree [2], are, respectively, −30.2 and −45. Pitzer [21] gives −30.3 as the standard entropy change for the second dissociation of phosphoric acid.

[d] Pitzer [21] measured the heat of ionization and computed the entropy from the thermodynamic relation $\Delta S° = (\Delta H° - \Delta F°)/T$. For the dissociation of bisulfate and bicarbonate ions, $\Delta F°$ at 25° C was taken from the emf measurements of Hamer [27] and of MacInnes and Belcher [28], respectively.

V. pH VALUES OF PHENOLSULFONATE SOLUTIONS

1. CALCULATION OF THE pH VALUES FROM ELECTROMOTIVE-FORCE MEASUREMENTS

The pH value of each buffer solution was computed directly from the emf by eq 8, with the use of an a_i value of 8 Å the β values given in table 3. The pH values are listed in tables 7 and 8. The change of pH with temperature of four buffers of series A is shown in figure

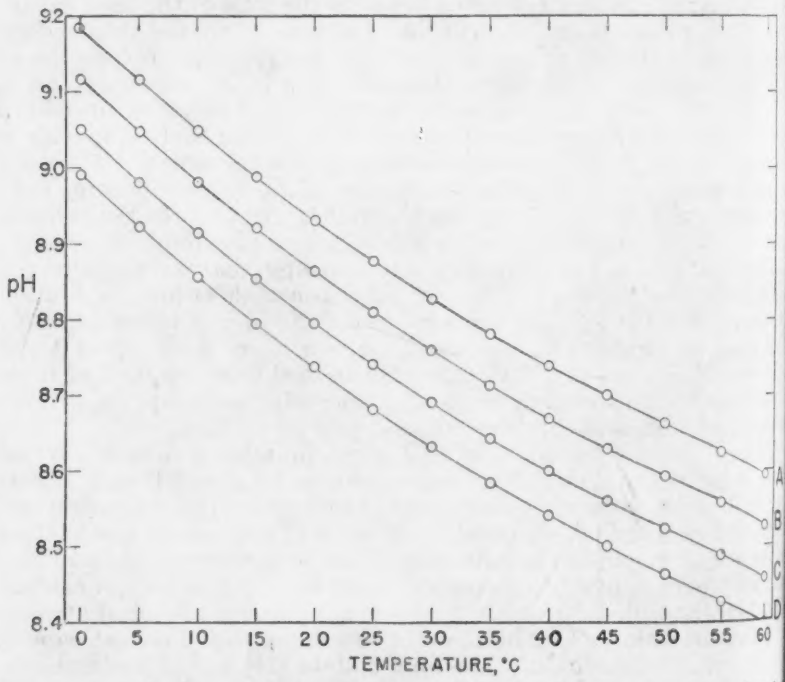

FIGURE 4.—pH *values of four phenolsulfonate-chloride solutions plotted as a function of temperature.*

Curves *A*, *B*, *C*, and *D* represent, respectively, solutions A8, A5, A3, and A1.

4. Curves *A*, *B*, *C*, and *D* represent respectively solutions A8, A5, A3, and A1.

Each of these solutions is a suitable standard for pH. The buffer capacity of the most dilute buffers, however, is fairly low. These solutions are more susceptible to errors in pH caused by the absorption of carbon dioxide from the air, by alkali from glass bottles in which they may be stored, and by dilution than are the buffers whose component salts are at least 0.01 *m*.

TABLE 7.—pH *values of mixtures of potassium p-phenolsulfonate* (m_1), *potassium sodium p-phenolate sulfonate* (m_2), *and sodium chloride* (m_3): *series A and B*

Solution number	m_1	m_2	m_3	pH				
				0°	5°	10°	15°	20°
A1	0.09628	0.09744	0.09622	8.992	8.923	8.857	8.795	8.738
A2	.05979	.06051	.05975	9.024	8.956	8.889	8.828	8.770
A3	.04130	.04180	.04127	9.051	8.981	8.915	8.854	8.796
A4	.03070	.03107	.03068	9.072	9.003	8.937	8.876	8.818
A5	.016220	.016416	.016210	9.116	9.048	8.982	8.922	8.865
A6	.009425	.009539	.009419	9.154	9.085	9.025	8.959	8.901
A7	.007710	.007803	.007705	9.168	9.101	9.035	8.975	8.918
A8	.005805	.005875	.005801	9.184	9.115	9.050	8.989	8.932
A9	.003703	.003748	.003701	9.210	9.141	9.076	9.016	8.958
A10	.09780	.09873	.09761	8.993	8.924	8.856	8.793	8.738
A11	.06503	.06565	.06491	9.019	8.952	8.884	8.822	8.764
A12	.05321	.05371	.05311	9.033	8.964	8.897	8.835	8.777
A13	.03944	.03982	.03937	9.055	8.985	8.919	8.856	8.799
A14	.017758	.017927	.017724	9.110	9.041	8.975	8.913	8.856
A15	.016094	.016248	.016063	9.116	9.047	8.980	8.919	8.861
A16	.008621	.008703	.008604	9.156	9.087	9.021	8.960	8.903
A17	.003723	.003758	.003716	9.206	9.138	9.072	9.012	8.955
B1	.07306	.09859	.10110	9.120	9.051	8.985	8.923	8.866
B2	.04951	.06682	.06851	9.148	9.076	9.010	8.949	8.890
B3	.04269	.05761	.05907	9.157	9.085	9.019	8.958	8.899
B4	.02465	.03326	.03411	9.199	9.124	9.058	8.997	8.939
B5	.012009	.016207	.016618					
B6	.010339	.013953	.014307	9.254	9.185	9.120	9.058	9.000
B7	.006241	.008422	.008636	9.292	9.222	9.157	9.096	9.038

	pH							
	25°	30°	35°	40°	45°	50°	55°	60°
A1	8.682	8.633	8.585	8.542	8.502	8.464	8.427	8.395
A2	8.715	8.665	8.618	8.575	8.535	8.498	8.461	8.429
A3	8.741	8.691	8.644	8.601	8.561	8.524	8.489	8.456
A4	8.763	8.713	8.667	8.624	8.584	8.547	8.511	8.479
A5	8.810	8.760	8.714	8.671	8.630	8.594	8.558	8.526
A6	8.848	8.797	8.751	8.709	8.669	8.632	8.595	8.564
A7	8.863	8.816	8.769	8.727	8.687	8.651	8.616	8.584
A8	8.878	8.828	8.783	8.740	8.701	8.664	8.625	8.594
A9	8.904	8.856	8.810	8.767	8.726	8.689	8.652	8.618
A10	8.682	8.633	8.585	8.541	8.501	8.463	8.425	8.393
A11	8.709	8.660	8.613	8.570	8.530	8.492	8.455	8.423
A12	8.722	8.673	8.626	8.583	8.543	8.506	8.469	8.438
A13	8.744	8.695	8.648	8.606	8.565	8.529	8.492	8.460
A14	8.802	8.752	8.706	8.664	8.623	8.587	8.551	8.519
A15	8.807	8.758	8.711	8.669	8.628	8.591	8.556	8.525
A16	8.850	8.797	8.751	8.709	8.669	8.632	8.596	8.566
A17	8.900	8.850	8.806	8.762	8.722	8.683	8.647	8.613
B1	8.810	8.759	8.713	8.668	8.629	8.592	8.554	8.522
B2	8.836	8.786	8.740	8.696	8.656	8.619	8.583	8.551
B3	8.847	8.798	8.750	8.706	8.666	8.629	8.593	8.561
B4	8.885	8.835	8.787	8.744	8.704	8.667	8.630	8.598
B5	8.936							
B6	8.947							
B7	8.984	8.936	8.890	8.843	8.802	8.766	8.730	8.697

TABLE 8.—pH *values of mixtures of potassium p-phenolsulfonate* (m_1), *potassium sodium p-phenolate sulfonate* (m_2), *and sodium chloride* (m_3): *series C and D*

Solution number	m_1	m_2	m_3	pH				
				0°	5°	10°	15°	20°
C1	0.10283	0.09802	0.04977	8.973	8.904	8.837	8.770	8.717
C2	.08011	.07636	.05003	8.990	8.919	8.854	8.790	8.734
C3	.06418	.06118	.05003	9.003	8.933	8.869	8.806	8.747
C4	.05087	.04849	.05003	9.014	8.944	8.879	8.818	8.759
C5	.03578	.03411	.05003	9.029	8.962	8.898	8.836	8.778
C6	.015343	.014625	.05003	9.065	8.995	8.930	8.868	8.809
C7	.009787	.009329	.05003	9.084	9.014	8.949	8.888	8.829
D1	.06582	.09822	.04822	9.174	9.105	9.040	8.976	8.919
D2	.04580	.06834	.04824	9.194	9.124	9.059	8.996	8.939
D3	.03314	.04945	.04824	9.213	9.143	9.078	9.016	8.958
D4	.02682	.04002	.04825	9.224	9.155	9.090	9.028	8.969
D5	.02193	.03272	.04826	9.234	9.165	9.100	9.038	8.979
D6	.012187	.018186	.04826	9.257	9.188	9.123	9.060	9.002
D7	.006540	.009760	.04827	9.281	9.211	9.145	9.084	9.026
D8	.006003	.008958	.04827	9.282	9.211	9.145	9.084	9.025

	pH							
	25°	30°	35°	40°	45°	50°	55°	60°
C1	8.660	8.610	8.564	8.521	8.481	8.444	8.407	8.376
C2	8.678	8.627	8.578	8.537	8.497	8.460	8.423	8.391
C3	8.692	8.641	8.594	8.551	8.511	8.474	8.436	8.405
C4	8.703	8.653	8.606	8.563	8.526	8.487	8.450	8.418
C5	8.722	8.672	8.626	8.582	8.542	8.505	8.469	8.438
C6	8.755	8.709	8.658	8.615	8.576	8.538	8.503	8.471
C7	8.774	8.724	8.678	8.633	8.593	8.556	8.520	8.487
D1	8.864	8.815	8.767	8.725	8.683	8.646	8.609	8.576
D2	8.887	8.834	8.787	8.745	8.704	8.667	8.630	8.598
D3	8.903	8.853	8.806	8.763	8.722	8.686	8.649	8.616
D4	8.914	8.864	8.818	8.775	8.734	8.697	8.661	8.629
D5	8.924	8.875	8.828	8.785	8.744	8.707	8.671	8.640
D6	8.948	8.897	8.850	8.807	8.767	8.729	8.693	8.661
D7	8.971	8.921	8.874	8.831	8.790	8.753	8.717	8.684
D8	8.971							

The reproducibility of the pH values in the tables is about ±0.002 unit, an amount which corresponds with an uncertainty of 0.12 mv in emf. This uncertainty may be divided between experimental error in emf (±0.001 unit, or 0.06 mv) and errors in the molalities of the solutions, resulting from accidental errors in the preparation of the solutions and from unrecognized impurities (±0.001 unit). A further uncertainty of 0.001 unit is introduced with $E°$ and k. The estimated uncertainty of 0.2 A in a_t corresponds to about 0.002 unit in pH for the most concentrated solution studied, but this error diminishes rapidly as the ionic strength is lowered. It is impossible at present to estimate the absolute accuracy of a pH value. The validity of the assumption upon which the calculation of the activity coefficient of chloride ion rests has not been established.

2. STANDARD BUFFER SOLUTIONS

For the computation of the pH values of phenolsulfonate-chloride solutions other than those actually studied in this investigation, it is convenient to employ the equilibrium expression for the second dissociation in the logarithmic form, with the substitution of eq 3 for each activity coefficient:

$$\mathrm{pH}=\mathrm{p}K_2-\log\,(m_{\mathrm{HPs}}/m_{\mathrm{Ps}})-3A\sqrt{\mu}/(1+8B\sqrt{\mu}). \qquad (13)$$

The correction for hydrolysis is made quite readily by means of eq 9; m_{OH} for use in this equation is obtained from the stoichiometrical ratio, m_1/m_2, of potassium *p*-phenolsulfonate to potassium sodium *p*-phenolate sulfonate by means of the approximation:

$$m_{OH} \approx (K_W K_2)/(m_1/m_2). \quad (14)$$

This expression can be used with an error of less than 0.001 pH unit for all solutions in which the molality of each of the buffer salts exceeds 0.01. The values of pK_2, $3A$, $8B$, and K_W/K_2 are found in tables 3 and 4, and μ is computed from eq 11.

The pH values computed from eq 13 will be consistent within ± 0.002 unit with the emf measurements, if the buffer solutions meet the following requirements: (a) the ratio m_1/m_2 is between 2/3 and 1, (b) the molality of sodium chloride, m_3, is either approximately equal to the molality of potassium sodium *p*-phenolate sulfonate, m_2, or is 0.05, and (c) the temperature is between 0° and 60° C. The change of pH with temperature is larger, in general, for alkaline buffers than for acid buffers. For a change of 5 degrees, the last term on the right of eq 13 changes less than 0.003, whereas the molality term remains practically unaltered. The change in pH is, then, substantially the same as the change of pK_2 with temperature, or about 0.01 pH unit per degree.

The pH values at 25° C of the 17 buffer solutions of series A have been calculated by eq 13 and are compared in table 9 with those computed by eq 8 from the individual emf values. The average difference between the two sets of pH values is less than 0.001 unit. It should be emphasized that this agreement does not establish the validity of the assumptions discussed earlier in this paper. It demonstrates, however, the applicability of eq 3 to the experimental data.

TABLE 9.—*Comparision of* pH *values for series A buffers at 25° C calculated from* pK_2 *(eq 13) with those derived from the emf by eq 8*

Solution number	pH (eq 13)	pH (eq 8)	Solution number	pH (eq 13)	pH (eq 8)
A1	8.683	8.682	A10	8.681	8.682
A2	8.715	8.715	A11	8.709	8.709
A3	8.741	8.741	A12	8.722	8.722
A4	8.763	8.763	A13	8.744	8.744
A5	8.809	8.810	A14	8.802	8.802
A6	8.846	8.848	A15	8.808	8.807
A7	8.859	8.863	A16	8.850	8.850
A8	8.877	8.878	A17	8.902	8.900
A9	8.903	8.904			

In the practical determination of pH by electrometric methods, the electrode system is usually standardized by means of buffer solutions of known acidity. Phenolsulfonate solutions are most satisfactory as pH standards when the molality of each constituent of the buffer is between 0.01 and 0.05. With the use of eq 13, the pH values of a phenolsulfonate buffer in which the molalities of the phenolsulfonate, phenolate sulfonate, and chloride ions are each 0.025 have been computed and are given in table 10. This solution is prepared most conveniently by dissolving 0.05 mole (10.613 g) of potassium *p*-phenolsulfonate and 0.025 mole (1.461 g) of sodium chloride in sufficient carbonate-free sodium hydroxide solution to contain 0.025 mole of

alkali. The solution is then diluted with freshly boiled water to a volume of 1,000 ml. These directions yield a buffer solution in which the component salts are each 0.025 molar, instead of 0.025 molal. This difference of about 1 percent in concentration of each constituent is entirely permissible for, as table 7 shows, a dilution of 1 percent changes the pH value of such a buffer by less than 0.001 unit.

TABLE 10.—*pH values of the buffer solution composed of potassium p-phenolsulfonate, potassium sodium p-phenolate sulfonate, and sodium chloride, each at a molality of 0.025*

t	pH	t	pH
°C		°C	
0	9.082	35	8.676
5	9.012	40	8.633
10	8.946	45	8.593
15	8.884	50	8.556
20	8.827	55	8.520
25	8.773	60	8.488
30	8.723		

If a precision of ± 0.002 pH unit is desired, the purity of the phenolsulfonate must be assured either by analysis and recrystallization, if necessary, or by the use of a certified sample. Whereas an inert impurity present in amounts less than 0.6 percent will alter the pH by less than 0.002 unit, the presence of half that amount of free phenolsulfonic acid, for example, is sufficient to change it by the same margin. It is unlikely that the small amounts of phenol and potassium bisulfate formed by the hydrolytic breakdown of the salt at 110°, or in solution at the higher temperatures (40° to 60° C), would have a large effect on the pH value.

These standard buffer solutions should be protected carefully from contamination with carbon dioxide. They are best preserved in bottles of alkali-resistant glass. Until the stability of phenolsulfonate solutions has been thoroughly investigated, these buffers should be protected from direct sunlight and should be renewed frequently.

The authors are indebted to E. E. Sager for the purification of a portion of the potassium phenolsulfonate, to C. G. Malmberg for measuring the conductance of the water used in the preparation of the buffers, and to K. D. Fleischer for the carbon, hydrogen, and sulfur analyses of the salt.

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WASHINGTON, May 25, 1943.

U. S. Department of Commerce National Bureau of Standards
RESEARCH PAPER RP1560
Part of Journal of Research of the National Bureau of Standards, Volume 31, October 1943

X-RAY PATTERNS OF HYDRATED CALCIUM SILICATES

By Howard F. McMurdie and Einar P. Flint

ABSTRACT

X-ray powder diffraction data of 15 hydrated calcium silicates are reported as a supplement to a previously published report on the formation of these compounds. These data may be useful to workers on portland cement hydration, boiler scale, etc., for the identification of phases.

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I. INTRODUCTION

Some years ago a report [1] was published on the hydrothermal synthesis of hydrated calcium silicates. In the course of that study the crystalline products of hydrothermal action were identified in part by means of X-ray powder patterns. While the patterns made then were satisfactory for the purpose, they were not considered sufficiently sharp and accurate to justify measuring and reproducing the resultant data in the paper.

Since that time, however, there has been considerable interest in the hydrated calcium silicates because of their occurrence in the hydration products of portland cement, in boiler scales, etc. Therefore, the patterns of the compounds were remade on more modern equipment and the data are given here.

II. METHODS AND SOURCES OF MATERIALS

Of the 15 calcium silicate hydrates considered here seven occur as natural minerals, and these natural minerals were used to prepare the patterns. The other eight compounds were formed as described in the paper referred to above.[2]

Table 1 gives the source of the minerals and the starting material and subsequent treatment of the synthetic preparations. The experi-

[1] Einar P. Flint, Howard F. McMurdie, and Lansing S. Wells, *Formation of hydrated calcium silicates at elevated temperatures and pressures*, J. Research NBS 21, 617 (1938) RP1147.

[2] In the original paper, table 11, the compound $10CaO.5SiO_2.6H_2O$ is indicated as not being obtained synthetically. This is an error. It was made synthetically; in fact, it has not been found as a mineral.

ment numbers from the previous paper are also given and in that paper a complete discussion of the methods used is presented. Some of these phases were made at the time of the previous study, others were remade, and all were examined with the petrographic microscope to assure reasonable purity.

The patterns were registered with cameras of about 5.7-cm radius, using CuKα radiation.

TABLE 1.—*Origin of materials used in making the X-ray patterns*

A. MINERALS

Mineral	Composition	Place of origin
Okenite	$CaO.2SiO_2.2H_2O$	Discos Island, Greenland.
Gyrolite	$2CaO.3SiO_2.2H_2O$	Benkoelen, Sumatra, Netherlands East Indies.
Xonotlite	$5CaO.5SiO_2.H_2O$	Isle Royale, Mich.
Crestmoreite	$2CAO.2SiO_2.3H_2O$	Crestmore, Riverside County, Calif.
Foshagite	$5CaO.3SiO_2.3H_2O$	Do.
Afwillite	$3CaO.2SiO_2.3H_2O$	Dutoitspan Mine, Kimberley, South Africa.
Hillebrandite	$2CaO.SiO_2.H_2O$	Velardena District, Durango, Mexico.

B. SYNTHETIC PREPARATIONS

Composition	Method of preparation				Experiment No.[a]
	Starting material	Temperature	Pressure	Time	
		°C	atm		
$4CaO.5SiO_2.5H_2O$	$0.80CaO.SiO_2$ aq	225	25	14 days	20
$CaO.SiO_2.H_2O$	$CaO.SiO_2$ aq	150	5	60 days	28
$6CaO.4SiO_2.3H_2O$	$\beta 2CaO.SiO_2$	25	1	10 years [b]	61
$2CaO.SiO_2.H_2O$ [c]	$2CaO.SiO_2$ aq	225	25	44 days	63
2CA. $OSiO_2.H_2O$ [d]	$\beta 2CaO.SiO_2$	250	39	15 days	65
$10CaO.5SiO_2.6H_2O$	$\beta 2CaO.SiO_2$	200	15	3 days	66
$6CaO.3SiO_2.2H_2O$	$10CaO.5SiO_2.6H_2O$	450	400	7 days	70
$3CaO.SiO_2.2H_2O$	$3CaO.SiO_2$	250	39	12 days	75

[a] Experiment numbers from previous paper (J. Research NBS **21**, 617 (1938) RP1147).
[b] Later treated at 175° C in bomb for 41 days.
[c] Index of refraction = 1.60.
[d] Index of refraction = 1.64.

III. RESULTS

Table 2 gives the interplanar spacings (d) and estimated relative intensities for 15 calcium silicate hydrates. These compounds all have symmetry which is orthorhombic or lower; therefore, it is all but impossible to index the reflections.

TABLE 2.—*Diffraction data of 15 hydrated calcium silicates*

Estimated [1] intensity	d
Okenite (CaO.2SiO₂.2H₂O)	
	A
VS	8.91
W	7.67
VW	6.63
VW	4.22
M	3.59
M	3.09
M	2.99
S	2.96
S	2.83
VW	2.73
VW	2.57
VW	2.41
W	2.16
VW	1.897
M	1.823
Gyrolite (2CaO.3SiO₂.H₂O)	
M	9.6
W	7.9
W	6.4
W	4.68
S	4.24
M	3.84
W	3.54
VS	3.36
M	3.15
VW	3.02
VW	2.92
S	2.85
M	2.65
VW	2.58
VW	2.52
W	2.45
W	2.29
M	2.25
W	2.12
W	2.095
VW	2.060
VW	1.990
VW	1.940
S	1.884
M	1.813
Xonotlite (5CaO.5SiO₂.H₂O)	
M	7.10
S	4.22
VS	3.61
S	3.24
S	3.07
M	2.82
M	2.68
VW	2.62
M	2.49
W	2.41
W	2.25
S	2.03
S	1.940
M	1.826
W	1.748
M	1.705
W	1.679

Estimated [1] intensity	d
Crestmoreite (2CaO.2SiO₂.3H₂O)	
	A
M	14.9
S	10.4
W	5.5
W	4.9
VW	4.14
W	3.74
M	3.50
VW	3.29
VS	3.09
S	2.95
VS	2.84
M	2.74
W	2.66
VW	2.34
W	2.26
VW	2.18
W	2.05
M	1.959
M	1.861
M	1.819
VW	1.792
W	1.773
W	1.735
Foshagite (5CaO.3SiO₂.3H₂O)	
M	9.7
M	8.0
M	5.67
M	5.06
M	3.42
S	3.36
M	3.24
W	3.09
S	2.93
S	2.81
M	2.72
W	2.48
VS	2.31
S	2.16
W	2.11
W	2.073
W	2.040
W	1.950
VW	1.916
W	1.827
W	1.776
S	1.745
Afwillite (3CaO.2SiO₂.3H₂O)	
S	6.5
M	5.06
W	4.68
W	4.18
VW	3.76
VS	3.17
VW	3.05
VS	2.85
S	2.74
W	2.66
W	2.59
VW	2.44
M	2.36
VW	2.33
VW	2.275
M	2.159

Estimated [1] intensity	d
Afwillite 3CaO.2SiO₂.3H₂O—Con.	
	A
VW	2.065
W	2.026
W	1.988
M	1.955
W	1.924
W	1.868
M	1.808
M	1.782
VW	1.735
W	1.705
W	1.679
W	1.629
M	1.606
M	1.596
W	1.564
Hillebrandite (2CaO.SiO₂.H₂O)	
S	12.6
M	4.77
VW	4.05
VW	3.52
M	3.34
M	3.01
VS	2.92
VW	2.83
VW	2.75
VW	2.68
VW	2.62
VW	2.45
M	2.373
M	2.247
W	2.056
M	1.963
W	1.928
M	1.864
M	1.812
W	1.747
4CaO.5SiO₂.5H₂O	
S	4.22
W	3.76
M	3.14
S	3.05
W	2.85
VW	2.67
W	2.52
W	2.30
M	2.105
M	1.924
W	1.877
M	1.841
CaO.SiO₂.H₂O	
VW	6.13
W	4.52
W	4.24
VW	3.80
W	3.58
M	3.21
VS	3.01

Estimated [1] intensity	d
CaO.SiO₂.H₂C—Continued	
	A
M	2.78
M	2.50
S	2.23
VW	2.116
W	2.013
S	1.893
VW	1.868
VW	1.808
M	1.772
VW	1.632
W	1.601
6CaO.4SiO₂.3H₂O	
M	4.30
W	3.68
W	3.45
VW	3.39
M	3.22
VS	3.10
W	2.98
VW	2.94
W	2.86
W	2.73
W	2.64
W	2.58
S	2.253
S	2.066
W	2.034
VW	1.987
M	1.943
VW	1.897
W	1.833
W	1.792
W	1.756
S	1.699
2CaO.SiO₂.H₂O (n=1.60)	
W	4.83
M	4.26
W	3.55
W	3.38
W	3.28
S	3.05
VS	2.93
VW	2.42
W	2.40
W	2.24
W	2.07
M	1.963
M	1.875
M	1.819
W	1.637
2CaO.SiO₂.H₂O (n=1.64)	
W	4.22
VW	3.82
VS	3.04
M	2.84

[1] S, strong; M, medium; W, weak; V, very; B, broad.

TABLE 2.—*Diffraction data of 15 hydrated calcium silicates*—Continued

Estimated [1] intensity	d	Estimated [1] intensity	d	Estimated [1] intensity	d	Estimated [1] intensity	d
$2CaO.SiO_2.H_2O$ (n=1.64)—Con.		$10CaO.5SiO_2.6H_2O$ —Continued		$6CaO.3SiO_2.2H_2O$ —Continued		$6Ca$ $_2.2H_2O$ —Continued	
	A		*A*		*A*		*A*
S	2.70	W	2.66	VW	3.39	W	1.406
M	2.47	W	2.59	VW	3.30	M	1.270
W	2.35	VW	2.51	VW	3.23		
S	1.807	S	2.41	S	3.06	$3CaO.SiO_2.2H_2O$	
W	1.650	VW	2.32	M	2.96		
M	1.799	W	2.24	S	2.85		
W	1.732	W	2.15	VS	2.81	M	8.8
M	1.656	W–B	2.05	S	2.71	M	3.32
W	1.540	VW	1.98	M	2.607	M	3.03
M	1.264	W	1.950	S	2.535	VS	2.91
W	1.170	M	1.915	W	2.455	M	2.83
W	1.156	W	1.833	VW	2.404	W	2.47
		S	1.780	VW	2.349	VW	2.17
$10CaO.5SiO_2.6H_2O$		M	1.730	S	2.275	M	2.088
		M	1.706	M	2.22	VW	2.026
		S	1.649	W	2.169	W	1.996
VW	5.33			M	2.140	S	1.879
S	4.18			M	1.987	S	1.769
W	3.91	$6CaO.3SiO_2.2H_2O$		VW	1.951	M	1.696
M	3.53			VW	1.928	VW	1.667
S	3.27			VW	1.901	W	1.632
VW	3.05	W	6.64	W	1.738	M	1.573
M	2.89	W	4.63	M	1.708	W	1.506
M	2.80	W	4.24	W	1.670	W	1.438
W	2.72	W	3.79	M	1.634	W	1.366
				W	1.421		

[1] S, strong; M, medium; W, weak; V, very; B, broad.

The authors are indebted to W. F. Foshag and C. P. Henderson, of the U. S. National Museum, for samples of the naturally occurring minerals.

WASHINGTON, June 29, 1943.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1561

Part of Journal of Research of the National Bureau of Standards, Volume 31, October 1943

STRUCTURE OF THE WOOL FIBER AS REVEALED BY THE ELECTRON MICROSCOPE

By Charles W. Hock[1] and Howard F. McMurdie

ABSTRACT

An investigation of the wool fiber with the electron microscope was undertaken in order to get more data on the structure of the fiber and its constituent cells, and to correlate this information with results previously obtained by other methods. Specimens were prepared for examination by various physical and chemical procedures.

Over a wide range of magnifications the cortical cells always showed a distinctly fibrous structure. Whereas with the optical microscope only fibrils were observed within the cortical cells, the higher resolving power of the electron microscope made possible the resolution of still finer microfibrils. The scale cells, on the other hand, showed little internal organization. This difference in structure between the fibrous cortex and the nonfibrous or amorphous cuticle is believed to be of fundamental importance in interpreting many of the properties of the fibers.

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I. INTRODUCTION

Wool fibers are not simple homogeneous structures but consist of various parts and layers that become apparent under suitable conditions of observation. Thus a growing wool hair is found to have a bulbous root situated below the surface of the skin and a filamentous shaft that extends above the skin surface. The shaft, in turn, is made up of dead cellular units which are arranged in three layers—an outer layer of scales (cuticle), a middle region called the cortex, and a central core, or medulla. The medulla, which, in the finest grades of wool, is either very narrow or absent altogether, is not believed to contribute appreciably to the mechanical properties of the fibers, and attention accordingly has been directed largely to an understanding of the structure of the scale and cortical cells. The scales are restricted to a thin layer which constitutes the outer surface of the

[1] Research Associate at the National Bureau of Standards, representing the Textile Foundation.

fiber, whereas the cortex, either in the form of a solid or a hollow cylinder, depending on the extent of medullation, makes up the bulk of the fiber. A more detailed discussion of the microscopy of wool may be found in publications by Kronacher and Lodemann [1],[1] Von Bergen [2], Von Bergen and Kraus [3], Reumuth [4], Müller [5], Hock, Ramsey, and Harris [6], and others.

The principal chemical constituent of wool is keratin, a protein consisting essentially of long polypeptide chains connected laterally by disulfide cross-linkages [7, 8, 9, 10, 11]. Although both the cuticle and cortex appear to belong to this same general class of proteins, there is abundant evidence from various lines of investigation which indicates that there are, nevertheless, certain differences between them. For example, when wool is treated with enzymes the fibers are attacked first at their cut ends, where the enzymes have, presumably, easier access to the fiber. Prolongation of this treatment, moreover, causes the cortical cells to become separated from each other and ultimately released from the fiber, whereas the scales remain practically intact in the form of a hollow tube [6, 12]. Similarly, treatment of wool with reagents that cause swelling, such as sodium sulfide, shows that the scales are, as a rule, more resistant than the cells of the cortex [13, 14]. Likewise, it has been reported [15] that the passage of solutions of acid dyestuffs into the fiber is resisted by the cuticle. A consideration of staining and dyeing also reveals other differences between the scale and cortical layers. For example, when wool cells which have been separated by acids, alkalis, or enzymes, are treated with dyes such as methylene blue or orange II, only the cortical cells have any affinity for the stains [16, 17]. In like manner the work of Royer and Millson on dyed wool [18] shows that the ends of the fibers, which are not protected by scales, take up dye more rapidly than do intermediate parts of the fiber. This phenomenon is the basis of a number of tests for damage, in which the cortex colors only where previous injury to the scales allows entry of the test reagents [19, 20, 21]. A further difference between the scales and cortical cells is revealed by the Allwörden reaction, in which the scales, unlike the cells of the cortex, swell up into little sacs when the fibers are placed in a saturated aqueous solution of chlorine [22].

The most detailed information concerning the structure of the various types of wool cells is available as a result of investigations with the optical microscope. Using this technique, the principal difference between the cortical cells and the scales is the fibrous appearance of the former and the uniform or amorphous appearance of the latter—a difference which may be of fundamental importance. Since the dissimilarities in chemical composition of the cuticle and cortex are evidently slight [1, 17, 23, 24, 25], it seems probable that the differences in behavior of these two regions may be dependent more on physical than on chemical differences. Accordingly, it was thought interesting to note whether dissimilarities in structure are still observable at the high magnifications obtainable with the electron microscope, and the present study was undertaken to get more data on the structure of the wool fiber and its constituent cells and to correlate this information with results previously obtained by other methods.

[1] Figures in brackets indicate the literature references at the end of the paper.

II. APPARATUS AND MATERIALS

1. THE ELECTRON MICROSCOPE

The electron microscope used in this study was the Radio Corporation of America's type *B.* instrument, having electromagnetic lenses. Its construction and use, as well as that of electron microscopes in general, has already been discussed in various publications [26, 27]. It is important to recall, however, that the image produced by the electron microscope is the result of absorption and scattering of the electron beam, and that these effects are, in turn, a function of the density and thickness of the object. Thus the electron image is a result of differences in the amount and kind of matter traversed by the electrons and is not produced by differences in refractive index, as is usually the case in photomicrography.

Considerable caution must be exercised in interpreting electron micrographs. Since the instrument is evacuated during use, drying of the specimens ensues and this may bring about changes in structure, particularly in biological specimens. Furthermore, organic materials are sometimes disintegrated by the electrons, especially where thick sections absorb large amounts of electron energy. These, as well as other possible alterations which may occur during the preparation of the specimens for examination, should be borne clearly in mind.

2. SAMPLES OF WOOL

In order to have observations on a fairly representative number of wools, five different samples were used in the investigation. One sample of fine merino wool was the same as that used previously in this laboratory. It was purified by extractions with ethyl alcohol and with ether for 16 hours each, followed by washing with water at 40° C. The remaining wools had been given commercial degreasing treatments and were used just as received.

III. PREPARATION OF SPECIMENS

For a satisfactory examination with the electron microscope, specimens should not be more than a few tenths of a micron thick. Unfortunately, the finest wool fibers do not even approach this limit, so that various means must be used to obtain sections suitable for examination. Inasmuch as the methods of preparation may bring about changes in the structure of the specimens themselves, it seemed likely that the best understanding of the wool cells could be achieved by the examination of specimens that had been prepared by a variety of chemical and physical procedures. In the present investigation, specimens were prepared by the following four methods.

1. Untreated [3] and undamaged wool reacts slowly to enzymes, but it is unusually susceptible to attack if, for example, the disulfide cross-linkages have been ruptured by reduction with thioglycolic acid and then methylated to prevent reformation of the linkages [12]. After treatment with pepsin for several days to a week, cortical and scale cells are released from the wool fibers. For the present work, cells obtained by this procedure were washed repeatedly with distilled water until the suspension was neutral, whereupon a drop of the suspension was placed on the specimen holder of the microscope and

[3] In this discussion wool fibers that received no specific chemical treatments before being placed in enzymes will be designated *untreated* wool, whereas the fibers that were reduced and methylated before being subjected to the action of enzymes will be called *treated* wool.

allowed to dry. The scales were less than 0.5 micron in thickness and hence satisfactory for examination with the electron microscope. The cortical cells were too thick to allow passage of the electrons except at their tapering ends, and accordingly observations were confined principally to these regions.

2. Another method for obtaining scales for examination with the electron microscope involved treating the fibers with acid. Wool fibers were placed either in concentrated sulfuric acid for several hours or in concentrated formic acid for several weeks. This treatment loosened the scales and caused them to bend away from the fiber so as to resemble warped shingles on a roof. By subsequent agitation of the acid-treated fibers in a small amount of water, many scales and fragments thereof were removed. The released scales were washed with distilled water until neutral, and then examined in the usual manner. Although it is recognized that the acid treatment probably brings about changes in the structure of the scales, it is interesting to note that scales treated in this way still form Allwörden sacs when they are placed in chlorine water [6].

3. Mechanical separation of the scales from the fibers was accomplished by the method of King [28]. After attaching a weight to the fiber to keep it taut, the fiber was drawn across the edge of an ordinary glass slide mounted horizontally. In this way thin slivers were scraped off, and these sometimes appeared to consist solely of scale material.

4. Another method for obtaining scales by mechanical action involved the use of a Wiley mill. In this machine the fibers are cut lengthwise into rather long pieces which are, of course, too large and thick for examination. However, as the fibers pass through the mill, pieces of scale material are also broken and chipped from the surface of the fibers, and these fragments are suitable for use. In the microscope the thin scales were easily distinguished from the thick and dense pieces of fiber. Also, satisfactory specimens of cortical material were prepared by triturating the coarse powder from the mill between two pieces of ground glass.

IV. RESULTS AND DISCUSSION

1. STRUCTURE OF THE SCALE CELLS

Scales from five different samples of wool were examined at several magnifications. Although the structural pattern varied, depending on the differences in experimental technique, all the scales, regardless of the method of preparation or of the samples from which they came, showed certain similarities. For example, the margin of the distal part of the scale, i.e., the part away from the point of attachment and not covered by overlapping scales, was relatively thick and dense, and hence showed little evidence of a finer structure. The proximal end of the scale, on the other hand, was thin enough to allow passage of the electrons and thereby reveal details. Thus the scale as a whole is evidently wedge-shaped, decreasing in thickness from its distal to its proximal end.

The scales, unlike the cortical cells, show little internal organization even at the highest magnifications obtainable with the optical microscope. Usually this instrument shows clearly that the scales overlap in a manner comparable to that of shingles on a roof, but there is almost no indication of a pattern within the scales themselves

(fig. 1). The higher resolving power of the electron microscope, however, does reveal a pattern in the scales released by certain procedures. For example, figure 2 is an electron micrograph of part of a scale which had been prepared in exactly the same way as the scales shown in figure 1. The greater detail of the electron micrograph is evident, the scales appearing rather mottled, with less dense areas scattered throughout the denser regions. The less dense areas were irregular in shape, and varied in size up to about 1 micron. Generally speaking, all the scales separated from the fibers by chemical action had this mottled appearance. Specimens prepared by identical procedures did not, however, always have exactly the same appearance. Thus, although the scales obtained by treatment with sulfuric acid usually had a typical mottled appearance (fig. 3, *A*), occasionally they exhibited a more porous or vesiculate pattern (fig. 3, *B*). Likewise, the scales released by the action of untreated wool with pepsin often had the typical appearance of chemically released scales (fig. 4, *A*). Frequently, however, they underwent disintegration by the electrons, and then appeared as in figure 4, *B*.

Mechanically removed scales showed less structure than those separated by chemical techniques. At magnifications of only several thousand times they appeared uniform, with little indication of a finer structure. Sometimes at higher magnifications a faint pattern was discernible (fig. 5, *A*), but usually they still appeared structureless (fig. 5, *B*). For a number of reasons it seems likely that the relatively uniform and amorphous appearance of these scales approaches more closely the true structure than that observed in chemically released specimens. In the first place, mechanical action would seem to be less drastic than that of chemicals. Probably more significant, however, is the fact that indirect evidence from other lines of investigation suggest a type of structure with which that observed in the mechanically removed specimens is in agreement. For example, observations with the polarizing microscope reveal that, unlike the cortical cells, which are anisotropic, the scales have little if any birefringence [6]. Similarly, X-ray data by Astbury and Street [29] show that the X-ray spectrum of the cuticle, especially in the stretched condition, differs from that of the whole fiber, and suggests a more or less random orientation in the former. The stable nature of the scale material to dyes, swelling agents, enzymes, and many other reagents, has already been pointed, and is, likewise, compatible with the present observations.

2. STRUCTURE OF THE CORTICAL CELLS

The examination of cortical cells with the electron microscope confirmed and extended the results previously obtained with the optical microscope. With the latter instrument it has been shown that cortical cells are spindle-shaped and that they have a striated appearance, except for a granular nucleus (fig. 6, *A*). That the cells are fundamentally of fibrous structure, as indicted by their striated appearance, can be verified by dissecting single cortical cells with microneedles, whereupon numerous fibrils can be separated [6]. Between crossed nicols the fibrillate part of the cortical cell appears birefringent, whereas the granular nucleus does not (fig. 6, *B*).

Because of their size, observations with the electron microscope of the cortical cells released by pepsin were confined principally to their thin and tapering ends. But there are good reasons for believing that, except for the nucleus, they have a similar structure throughout. It

was found that over a wide range of magnifications the fibrous nature of these cells was still evident (figs. 7 and 8). However, whereas only fibrils were observed with the optical microscope, the electron microscope resolved still finer filaments, which, in the present investigation, will be called microfibrils. Zahn [30, 31] has similarly distinguished between fibrils and microfibrils in cortical cells. Figure 7, *B* shows the end of a cortical cell that has become frayed during preparation for examination. The separation of the fibrils (about 1 micron in width) from each other and their subdivision into microfibrils is also evident. Figure 8 represents part of another cortical cell at a higher magnification and in greater detail. The micrograph shows, essentially, parts of two fibrils, each made up of microfibrils and each connected to the other by additional microfibrils. The microfibrils, like the fibrils, appear not to be constant in width but to vary from a few hundred to about a thousand angstroms. Although the microfibrils are roughly parallel to the long axis of the cell, they do not present a picture comparable to a pile of matches in parallel alinement. They are observed, rather, to coalesce, so that apparent spaces of various sizes up to several tenths of a micron are formed between them. Adjacent fibrils are connected by other microfibrils which have a much looser texture. In other words, there are more microfibrils per unit area in the dense regions (fibrils) than in the less dense regions (interfibrillar regions) of the cortical cell.

The structural details revealed by the electron microscope make possible a clearer interpretation of previously observed phenomena. It seems likely, for example, that when cortical cells are dissected by means of microneedles, the needles first penetrate the interfibrillar regions, where the microfibrils are more easily disrupted than in the compact fibrils. Upon further manipulation, the interfibrillar regions apparently are torn longitudinally, thereby separating the fibrils. Also, as previously pointed out, the cortical cells are birefringent in the polarizing microscope (fig. 6, *B*). They are not, however, uniformly bright, but show alternate striations of high and low birefringence which appear to correspond to the fibrils and interfibrillar regions. From the present work with the electron micrsocope the fibrils might be expected to show greater brightness between crossed nicols because of the greater compactness of their microfibrils as compared with those in the interfibrillar regions. It should be borne in mind, however, that the light areas recorded on the micrographs, and which are especially abundant in the interfibrillar regions, do not necessarily indicate open spaces, but may only indicate areas which contain a material that is less dense than the surrounding microfibrils.

Upon examining specimens from reduced and methylated wool in the optical microscope, before and after their exposure to the electrons, there was no evidence that the cortical cells had been adversely affected by the electrons. Similarly, micrographs taken with the first flow of electrons through a specimen did not appear to differ from subsequent micrographs taken after longer bombardment. The behavior of cells from wool which had not been reduced was quite different. Just as soon as the beam of electrons struck these specimens, pronounced changes in structure occurred. The cells literally exploded and assumed a characteristic appearance (fig. 9). In the optical microscope the bombarded cells looked dark, charred, and distorted. This behavior, which is not uncommon with thick sections of organic

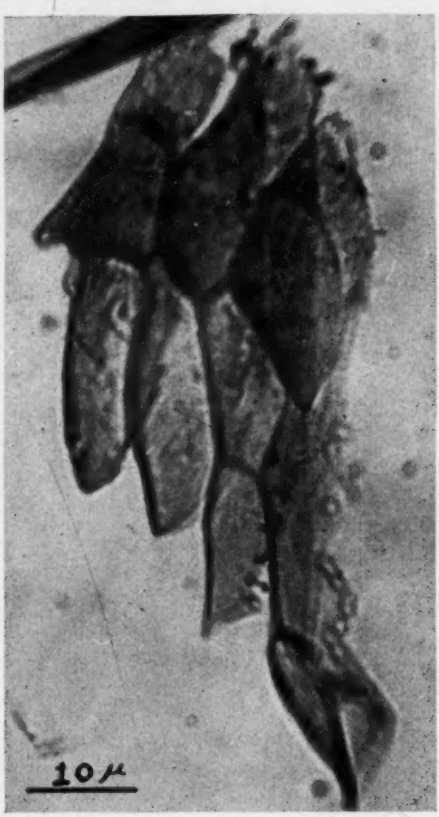

FIGURE 1.—*Group of scales released by the action of pepsin on treated wool fibers.*
Stained with orange II. Photomicrograph, ×1,500.

FIGURE 2.—*Part of a scale, released from treated wool by pepsin, showing its mottled appearance and fimbriate margin.*

Electron micrograph, ×16,000.

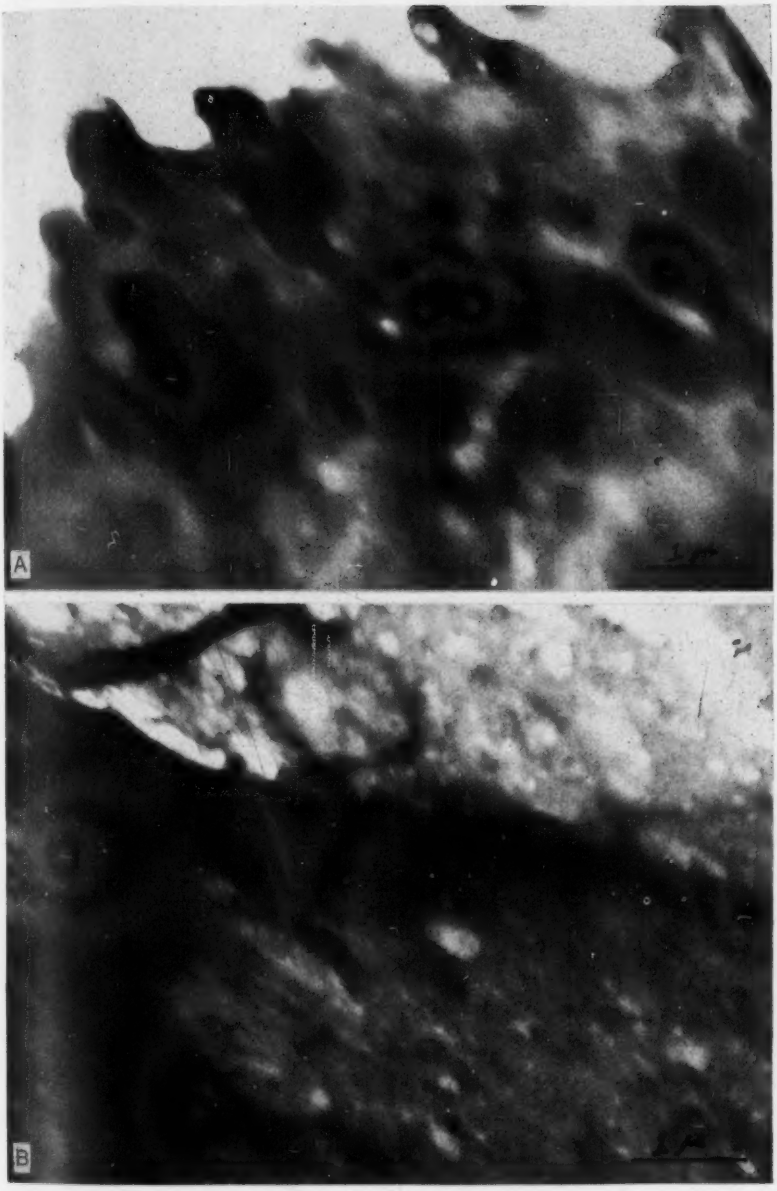

FIGURE 3.—*Scales obtained from wool by treatment with sulfuric acid.*

A, Proximal end of scale, having a mottled appearance. Electron micrograph, ×14,500. *B*, Parts of several adjoining scales, showing a vesiculate structure. Electron micrograph. ×15,500.

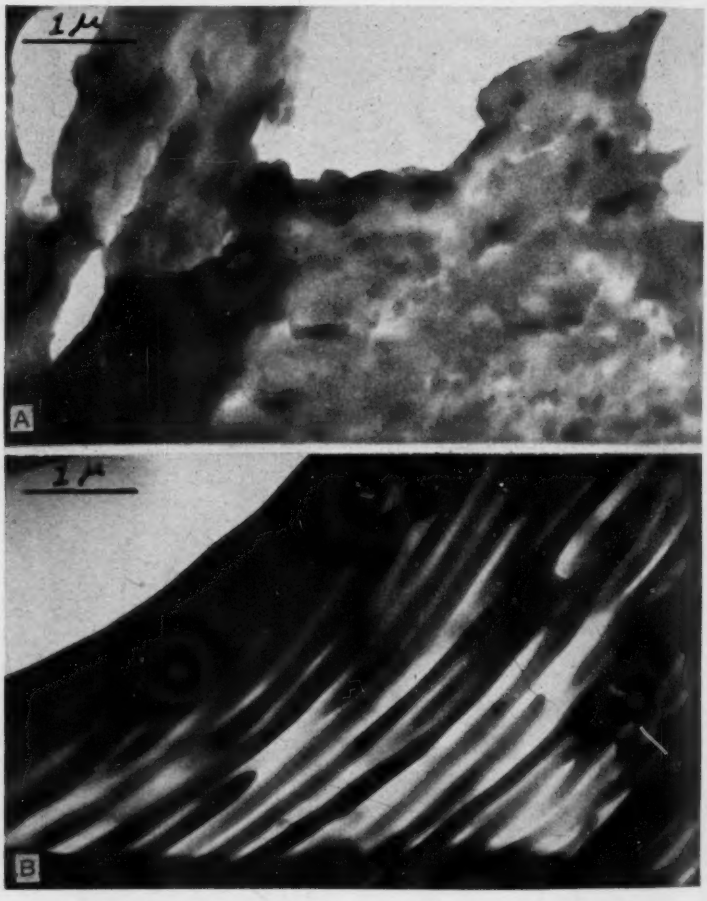

FIGURE 4.—*Scales released from untreated wool by pepsin.*

A, Part of scale, showing a mottled appearance. *B*, Part of scale which has undergone disintegration by the electrons. Electron micrograph, ×15,500.

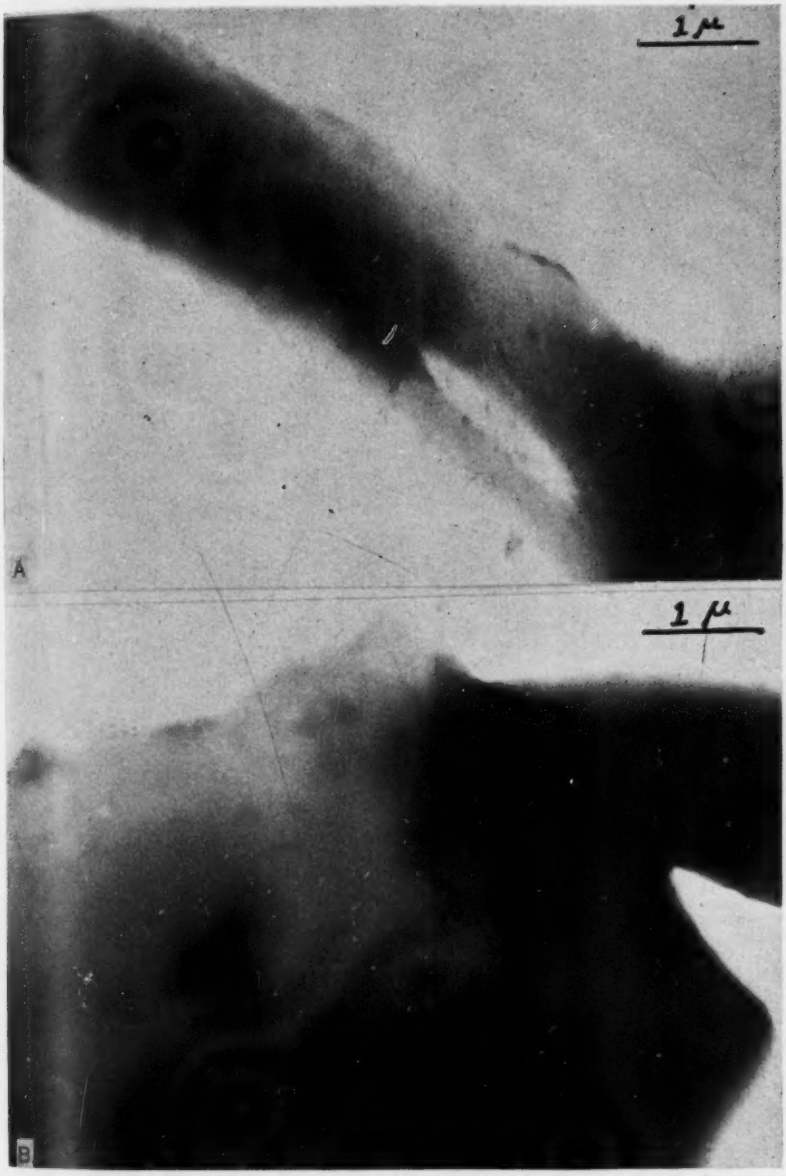

FIGURE 5.—*Parts of scales removed mechanically from fibers.*

A, Thin sliver of scale obtained from fiber by scraping. *B*, Piece of scale chipped off during passage of fiber through a Wiley mill. (The completely opaque parts of the micrograph are due to thick fragments of the cortex which cling to the scale.) Electron micrograph, ×16,500.

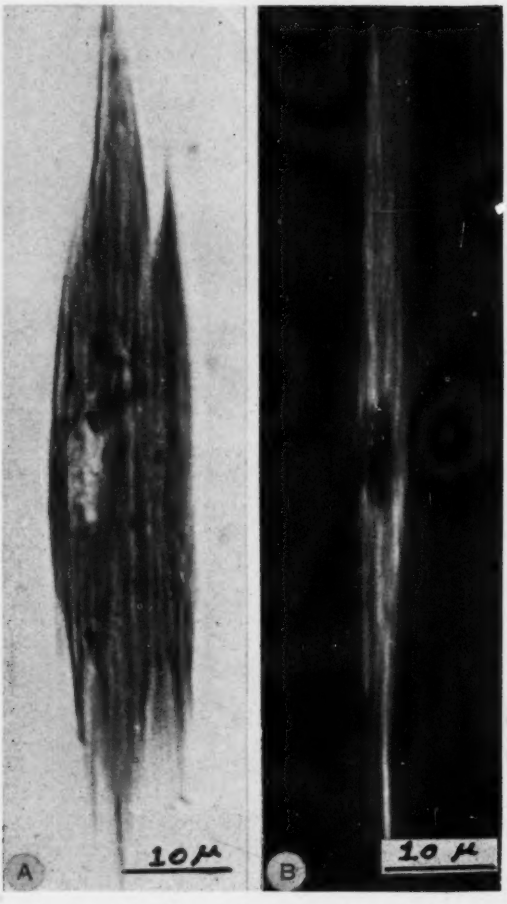

FIGURE 6.—*Cortical cells from treated wool.*

A, Single cell, showing the nucleus, and the fibrillate appearance of the rest of the cell. Stained with orange II. *B*, Single cell, between crossed nicols, showing the nonbirefringent nucleus in the birefringent cell. Photomicrograph, ×1,500.

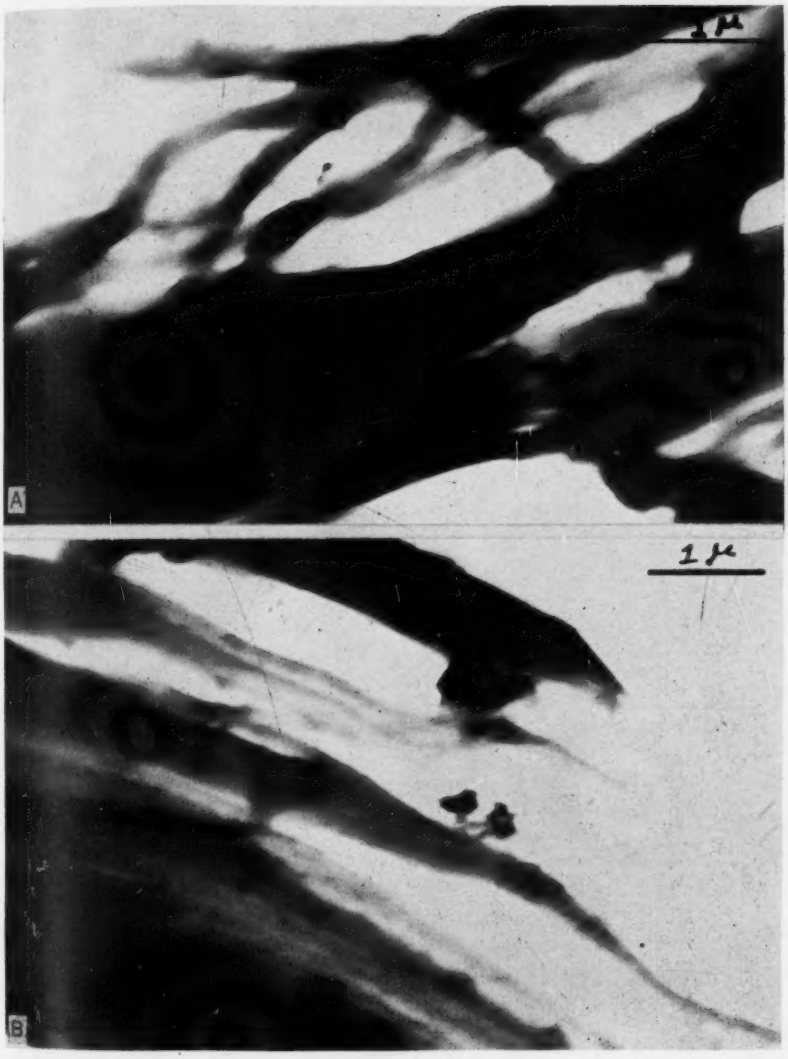

FIGURE 7.—*A and B are parts of cortical cells from treated wool, showing separation of the fibrils into still smaller microfibrils.*

Electron micrograph, ×16,000.

FIGURE 8.—*Part of cortical cell, showing fibrils and microfibrils.*
Electron micrograph, ×26,500.

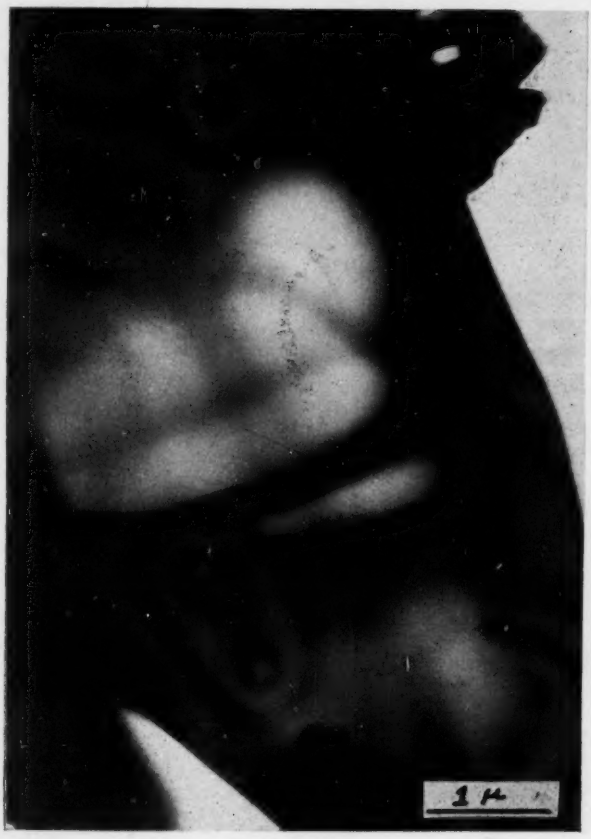

FIGURE 9.—*Part of a cortical cell disorganized by the electrons.*
Electron micrograph, ×17,000.

FIGURE 10.—*Part of cortex obtained by mechanical action.*
Portion of a cell showing microfibrils. Electron micrograph, ×20,000.

materials [32], has been described previously in the cotton fiber [33, 34].

The differences in reaction of the cells from untreated and from treated wool to bombardment by electrons make it interesting to speculate on the causes of this phenomenon. Since the specimens of wool used in this phase of the work were identical except for the reduction and methylation treatment, it seems probable that this treatment may account for the observed behavior.

Because of the thickness and density of the cortical cells, it may be expected that under bombardment by the electrons a large amount of energy would be absorbed, and this in turn would tend to disorganize the keratin. The foamy appearance of the disorganized cells suggests, moreover, that the decomposition may be accompanied by the evolution of gases. Consequently, a certain degree of breakdown might be expected to occur in cells from both the untreated and from the treated wool. However, in untreated wool the close alignment of the keratin molecules presumably does not permit the gases to diffuse readily, and as a result the cell explodes. The looser arrangement of the molecular chains in reduced and methylated wool, on the other hand, apparently allows diffusion to take place more easily and consequently disintegration does not occur. Also, in preparing the treated wool the disulfide cross-linkages are ruptured (reduced) and then methylated to prevent their re-formation. This may impart to the long polypeptide chains more freedom of movement when subjected to mechanical forces. In untreated wool, on the other hand, the original cross-linkages remain intact and thereby hold the keratin chains in rather rigid alinement.[4]

Although both scale and cortical cells from untreated wool usually underwent disintegration by the electrons, occasionally scales from the former were not disorganized (compare figs. 4, *A*, and 4, *B*). In these instances, the specimens presumably were thin enough for the electrons to pass through without disturbing the molecular architecture of the cell.

Additional explanations for the differences in behavior of these samples of wool during bombardment may also be suggested. It is possible, for instance, that the treatment with pepsin removed from the reduced and methylated wool some substance, thereby increasing the porosity of the treated wool as compared with the untreated wool. This difference in porosity might account for the observed differences in reaction. Similarly, the temperature at which disintregation of the specimens occurs may be lower for untreated than for treated wool, and this may be another explanation of the phenomenon. However, regardless of the specific reasons for the unlike behavior of these specimens in the electron microscope it is instructive to note that besides the differences which these wool fibers show in alkali-solubility, in mechanical properties, and in susceptibility to attack by enzymes and microorganisms, there is also this additional difference in the reaction of their component cells when exposed to electrons.

Cortical material which had received no specific chemical treatments, but which was prepared by trituration as previously described, was also examined for comparison with the cells released from wool by chemical action. Again, it was found that the cortex is made up of a highly fibrous material. Because the sections were prepared by rather

[4] Stress-strain measurements indicate that reduced and methylated fibers are capable of greater elongation than untreated fibers [35].

drastic mechanical action, and also because the plane of the sections is uncertain, a detailed interpretation of the micrographs is difficult. However, figure 10 shows what appears to be innumerable interlocking and variously aggregated microfibrils, and thereby gives further evidence of the fibrous nature of the cortical cells.

There is abundant evidence from chemical, physical, and microscopic studies, in support of a fundamental fibrous structure of textile fibers, and to this knowledge the present investigation of wool gives additional support. Whereas with the optical microscope only fibrils may be observed within the cortical cells, the electron microscope resolves still finer microfibrils. It is important to note, however, that studies with the electron microscope support previous evidence which indicates that only the cortex and not the cuticle appears to have a fibrous structure.

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WASHINGTON, August 9, 1943.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1562

Part of Journal of Research of the National Bureau of Standards, Volume 31, October 1943

A FRICTION METER FOR DETERMINING THE COEFFICIENT OF KINETIC FRICTION OF FABRICS

By Edwin C. Dreby [1]

ABSTRACT

A friction meter is described, and its application to the evaluation of the smoothness of a wide variety of fabrics is discussed. The ruggedness, sensitivity, and ease of operation of the instrument make it suitable for the routine testing of fabrics, the evaluation of finishing agents, and the control of finishing processes.

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I. INTRODUCTION

The frictional properties of textile fibers, yarns, and fabrics have to be taken into consideration by both manufacturers and users of fabrics. Fabric smoothness, "sheen," "creep," and wear are very important characteristics associated with the frictional properties of fabrics. The development of new fibers and finishing agents for fabrics creates a need for adequate means for evaluating their characteristics. To this end an investigation was undertaken jointly by the American Society for Testing Materials and the National Bureau of Standards for the development of methods for the evaluation of textile finishes. The work reported in this paper is concerned principally with the relation of frictional properties to the smoothness of fabrics and to "hand" or feel, in general. The friction meter described in this paper was developed for determining the coefficient of friction of fabrics. The device meets the requirements of ruggedness, sensitivity, and ease of operation desired of an instrument for routine textile testing.

One of the earliest recorded investigations of the frictional characteristics of fabrics was that of Rennie [1],[2] who measured the resistance to sliding and abrasion of several wool fabrics. Rennie used the sliding-

[1] Formerly Research Associate at the National Bureau of Standards, representing the American Society for Testing Materials.

[2] Figures in brackets indicate the literature references at the end of the paper.

block method, in which a fixed block is covered with one piece of the fabric to be tested and a weighted movable block is covered with another piece. The force just sufficient to overcome the resistance to sliding of one block on the other is then determined.

Two recent investigators have studied fabric friction and its relation to the slipperiness and smoothness of fabrics in the hands. Mercier [2] used the inclined-plane method in which a block covered with one piece of the fabric rests upon a sloping surface covered with another piece of the fabric. The tangent of the angle that the sloping surface makes with the horizontal when the block will just start to slide is taken to be the coefficient of friction. Morrow [3] developed a method for determining the coefficient of kinetic friction, in which a strip of the fabric was fastened on the rim of a wheel that was rotated at constant speed. Another strip of the cloth or some other material was mounted on a block that rested on the rim under known load. The frictional force was balanced by weights. Morrow determined the coefficient of kinetic friction of a fabric both against itself and against other surfaces.

The friction meter was devised to overcome a disadvantage common to the methods utilized by the previous investigators, namely that of having to balance the frictional force by varying the applied force by increments. Such a procedure requires numerous trials before the frictional force is balanced correctly. This disadvantage not only makes the measurement tedious but it also leads to unsatisfactory results, particularly for fabrics having a coefficient of static friction and a coefficient of kinetic friction of widely different magnitudes. With the friction meter, the frictional force is balanced continuously by spring tension so that all fabrics may be tested with a simple and identical technique. In addition the device has the ruggedness of construction and simplicity of design desired in a laboratory testing instrument.

In the present paper the construction and operation of the friction meter is described, and various factors affecting the measurement of the coefficient of friction and the relation of the coefficient of friction to the smoothness and hand of fabrics are discussed.

II. DESCRIPTION AND USE OF THE FRICTION METER

A sketch of the friction meter is given in figure 1. A horizontal table about 6 inches square, having a smooth surface, is located between a torsion element and a drum. The torsion element has a clamp for attaching one of a pair of fabric specimens required for a test. Deflections of the torsion element are indicated on a dial gage. The drum is provided with a clamp for attaching the other fabric specimen to it and a crank for winding the specimen on the drum. A metal block weighing 1 pound and having a lower surface 10 square inches in area (3 inches by 3⅓ inches) is provided [3] to subject the specimens to load.

In making a test, two specimens about 10 inches long and 3½ inches wide are cut from the fabric with the long dimension of each specimen in the direction of the fabric for which the coefficient of friction is

[3] Drawings showing the details of construction of the friction meter may be obtained from the National Bureau of Standards. A special committee of the American Society for Testing Materials has arranged for the manufacture of this machine for sale. Further information can be obtained from the chairman of the Special Committee, George A. Slowinske, E. I. du Pont de Nemours & Co., Inc., P. O. Box 386, Wilmington, Del.

desired. An end of one specimen is fastened in the clamp on the drum so that the fabric lies face up on the table of the instrument. An end of the other specimen is fastened in the clamp on the torsion element so that it lies face down on the specimen attached to the drum. The weight is placed centrally on top of the test specimens. The crank is then turned at a steady rate of approximately 30 revolutions per minute, thus drawing the lower specimen from under the upper one at a speed approximating 2½ feet per minute. The specimen is drawn through until its free end reaches the back edge of the weight and then,

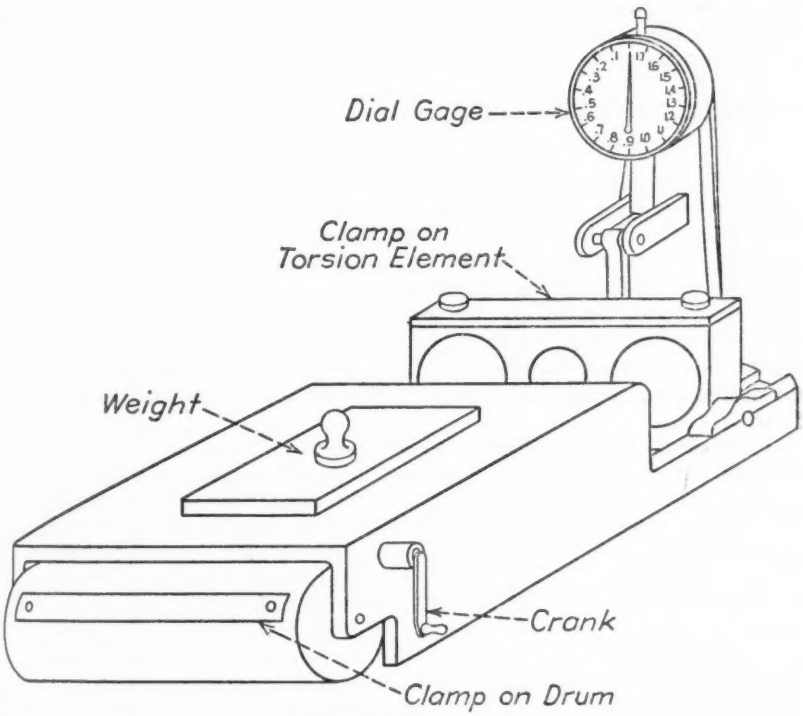

FIGURE 1.—*Friction Meter.*

without unclamping, the specimens are put back in their original positions and the process is repeated. The constant or nearly constant value indicated on the dial of the gage the second time the lower specimen is withdrawn is noted. This is taken to be the coefficient of kinetic friction of the fabric sliding on itself when the scale on the dial indicates the frictional force in pounds, as provided below, and the 1-pound load is used. The average of the results obtained by testing two pairs of specimens is sufficiently duplicable for most purposes, as is shown later.

III. CALIBRATION OF THE FRICTION METER

The friction meter was calibrated in a simple manner. A fine string was fastened in the clamp on the torsion element and passed over a low-friction pulley placed in front of the instrument so that it just cleared the table of the instrument. A pan for holding weights was

fastened to the free end of the string. Deflections of the dial gage were noted for a series of loads from 0 to 2 pounds, successive loads differing by ¼-pound increments. By applying slight hand pressure to the torsion element, deflections for specific loads were noted as the equilibrium point was approached from higher and lower values. With the well-lubricated, low-friction pulley that was used, the differences between the deflections for the two directions of approach were very small. The mean was taken. Within the range of calibration there was a linear relationship between the deflections of the torsion element and the applied loads. From the calibration obtained, a scale was made for the dial gage, indicating in pounds the force applied to the torsion element. The same scale indicates the coefficient of friction when the 1-pound weight is used for the load.

IV. FACTORS AFFECTING THE COEFFICIENT OF KINETIC FRICTION

The coefficient of kinetic friction between two bodies is the ratio of the force, applied parallel to the surfaces, required to cause one to slide over the other at a uniform speed to the force holding them together. For many substances, it is, within limits, independent of the area of the surfaces in contact and of the relative speeds of the surfaces. For irregular, compressible substances, such as fabrics, it is not independent of these factors. Other factors being constant, an increase in area causes a decrease in the coefficient or friction and an increase in speed causes an increase in the coefficient of friction of fabrics.

Variations in the coefficient of friction of fabrics resulting from these factors can be minimized by using a standard set of conditions for measuring all fabrics. As a result of tests with various weights, the use of the 1-pound weight with 10 square inches of bottom surface (giving a pressure of 0.1 pound per square inch) seemed most practical. The speed is controlled by hand, but tests have shown that speeds twice as great or half as great as that specified cause variations in the coefficient of friction of less than 5 percent. Since it is possible to control the speed within much smaller limits than these, differences in values due to this cause will be small and of the order of the variations in the results for different specimens from the same fabric, which are from 1 percent to 4 percent, depending upon the magnitude of the coefficient of friction.

Variables that might influence the results because of improper placing of the weight were investigated. Placing the weight at different positions other than the central position, dropping it in place, adding an additional load and removing it before the test, permitting the weight to rest on the specimens for different time intervals before making the test, and placing the weight on the specimen with a mechanical device to avoid impact, resulted in no more scattering of the results of individual tests than was obtained with the specified technique.

Several types of surfaces were tried in an attempt to establish a standard surface against which all fabrics may be measured. These included different fabric surfaces, two metal surfaces with different degrees of polish, and two leather surfaces. The coefficients of friction of some of these surfaces were not sufficiently constant or reproducible, and the range of results for series of fabrics tested against

a common surface was much smaller than the range when tested against their own surface. The greater sensitivity of the fabric against fabric method of measurement and the advantage of having a fresh surface for each measurement led to the testing of the fabric against itself in the studies made with the friction meter.

Figure 2 shows how the values of the coefficient of friction vary during the measurement and on successive remeasurements of a pair of specimens of cotton percale. At the start of relative motion a very high reading is obtained. This value varies over a considerable range for different specimens from the same fabric, being affected by

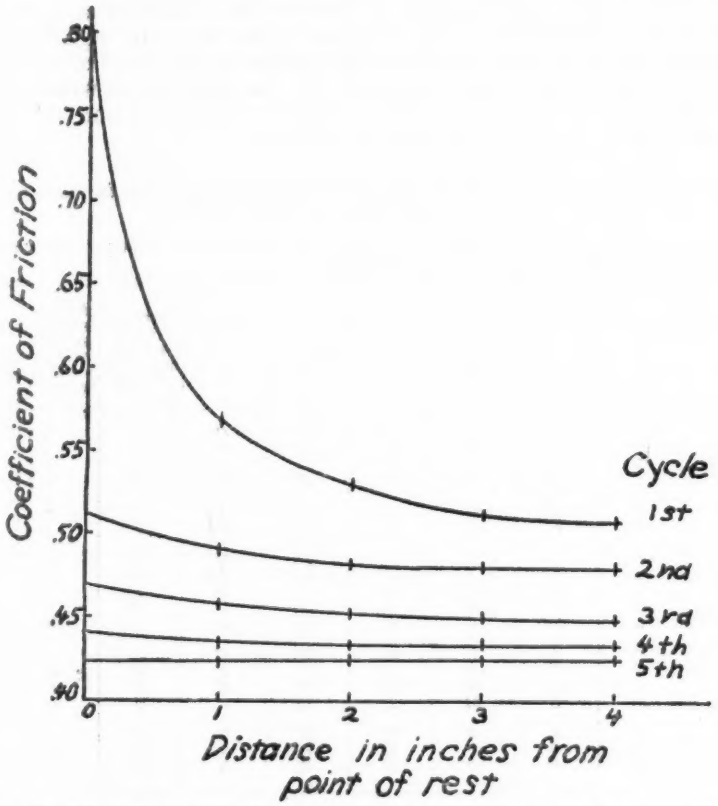

FIGURE 2.—*Variations in coefficient of friction during course of tests on an 80×80 cotton percale.*

the manner in which the weight is placed on the specimens and by small differences between the specimens. As soon as relative motion of the specimens is begun, the value drops rapidly and after a relative movement of 2 inches the value is almost constant. On remeasuring the specimen, the value is at first approximately the same as that near the end of the previous measurement. It drops to a more or less steady value, which is lower than that obtained in the first test. When the measurements are repeated further, with the same surfaces, the coefficient of kinetic friction drops slowly and continuously. This change in the coefficient of friction probably results from lining

up the projecting fibers and matting them into a smoother, more compact surface. The values of the coefficient of friction of cotton percales observed in the second test were the earliest values that were reproducible. Other fabrics gave results varying no more than these, and some fabrics, like smooth rayon twills or satins, gave results varying much less. Accordingly, the procedure of observing the coefficient during the second test was used for all fabrics.

V. DISCUSSION OF RESULTS OF MEASUREMENTS WITH THE FRICTION METER

The results of measurements of three series of fabrics are presented to show the sensitivity of the friction meter and the significance of the coefficient of kinetic friction with respect to the hand of the fabrics and also the finish of the fabrics. All the specimens were exposed for 24 hours in air of 65±2-percent relative humidity and 70°±2° F, and they were measured in this atmosphere.

TABLE 1.—*Coefficient of kinetic friction of 80×80 cotton percales in relation to their smoothness as judged by seven observers*

Fabrics are designated *A* to *R* in order of average smoothness rating, smooth to rough. Fabrics bracketed together were considered indistinguishable in smoothness.

Order of smoothness by observer							Average order of smoothness (7 observers)	Average relative smoothness rating (7 observers) [a]	Coefficient of kinetic friction [b]
1	2	3	4	5	6	7			
A	*A*	*A*	*D*	*A*	*C*	*C*	*A*	3.5	0.49
B	*D*	*F*	*E*	*C*	*B*	*E*	*B*	3.6	.49
C	*B*	*B*	*C*	*G*	*D*	*A*	*C*	3.8	.39
J	*G*	*G*	*B*	*D*	*J*	*B*	*D*	4.9	.39
D	*F*	*H*	*G*	*B*	*N*	*I*	*E*	6.1	.43
E	*E*	*K*	*K*	*L*	*A*	*F*	*F*	6.7	.53
F	*H*	*C*	*I*	*I*	*F*	*G*	*G*	6.9	.36
G	*I*	*E*	*A*	*F*	*H*	*H*	*H*	7.8	.46
H	*K*	*D*	*H*	*E*	*E*	*D*	*I*	9.1	.45
I	*C*	*P*	*F*	*J*	*K*	*J*	*J*	9.9	.40
M	*L*	*M*	*J*	*K*	*L*	*O*	*K*	10.0	.42
K	*O*	*I*	*L*	*H*	*M*	*M*	*L*	11.6	.43
L	*O*	*O*	*R*	*N*	*I*	*L*	*M*	12.4	.46
N	*P*	*N*	*N*	*M*	*O*	*K*	*N*	13.3	.53
P	*M*	*L*	*M*	*P*	*Q*	*P*	*O*	14.1	.50
O	*J*	*J*	*O*	*O*	*G*	*R*	*P*	14.5	.51
Q	*N*	*Q*	*P*	*Q*	*P*	*Q*	*Q*	16.0	.60
R	*R*	*R*	*Q*	*R*	*R*	*N*	*R*	16.9	.55
Average mean deviation								±2.35	±0.009

[a] Obtained by assigning numerical ratings of 1 to 18 to the fabrics in the order in which they were placed by the observers (from smooth to rough). The numbers for fabrics bracketed together were then averaged, and all fabrics in the bracket were given this average rating.
[b] Average of 2 determinations.

A series of eighteen 80×80 cotton percales, representing the products of 10 different manufacturers, were graded with respect to their relative smoothness by each of 7 textile experts. The fabrics were then numbered from 1 to 18 in the order in which they were placed by each expert, from smooth to rough, and these numbers were used as numerical ratings. The numbers of fabrics which were considered indistinguishable by an expert were averaged, and the average value was taken to be the numerical rating of those fabrics. The seven

individual relative ratings thus obtained for each fabric were averaged to give an average relative smoothness rating. The data and results are given in table 1. The mean deviation of the seven individual ratings was computed for each fabric. The average of these mean deviations was ± 2.35 units of rating.

The coefficients of kinetic friction of these fabrics were determined for duplicate pairs of specimens. The average mean deviation calculated as above was ± 0.009 unit of the coefficient of kinetic friction. The data are given in table 1.

The ratio of the spread of values obtained by each method to their average mean deviation is an indication of the number of distinct groups into which these fabrics might be divided by the methods of measurement. The ratio for the friction meter is about 27, for the smoothness ratings only 6. The friction meter is thus quite sensitive to differences in the fabrics. This was found to be true for other fabrics, and measurements indicated that two pairs of specimens of most fabrics would give a reliable result.

The correlation between the order of the eighteen 80×80 cotton percales determined by the tactual method and by the friction-meter method was computed by the method of Kendall.[4] It was 35 to 41 percent, depending upon the order of ranking of the fabrics whose coefficients of friction are the same. According to this statistical test, no clear correlation is indicated. It must be concluded that the coefficient of friction is not the only property of a fabric contributing to its smoothness.

Separate portions of an 80×80 and of a 68×72 print cloth were treated with different concentrations of each of two finishing agents. This method of treatment produced only small differences in the physical properties of the fabrics. Under these conditions there was a direct relationship between the coefficient of friction and the relative differences in smoothness, as shown by the results in table 2.

TABLE 2.—*Coefficients of kinetic friction of 80×80 and 68×72 cotton print cloth treated with different concentrations of two finishing agents*

Fabric treatment	Coefficient of kinetic friction		Tactual smoothness, (1) rough to (4) smooth
	80×80	68×72	
Untreated	0.61	0.64	1
1.0% of finish *A*	.56	.60	2
1.5% of finish *A*	.53	.59	3
2.0% of finish *A*	.52	.58	4
Untreated	.61	.64	1
1.0% of finish *B*	.54	.60	4
1.5% of finish *B*	.54	.60	3
2.0% of finish *B*	.55	.61	2

Various relations between flexibility and compressibility, the two other principal properties of a fabric affecting the judgment of hand, and the coefficient of friction which might give an evaluation of

[4] The Kendall coefficient of correlation between two series of rankings is given by the equation $2\Sigma/n(n-1)$, where n is the number of members ranked, and Σ is computed as follows: The members are put in objective order in the one series, which then determines the corresponding order of the rankings for the other series. Each member in turn of the latter sequence of rankings is compared with succeeding members in the sequence. Those pairs in the correct order are given a value of $+1$ and those in the inverted order are given a value of -1. The sum of these values is denoted Σ. The method is described in detail by Schwarz and Winn in "Technical Evaluation of Textile Finishing Treatments. III. Use of Rank Correlation for Comparison of Data." Am. Dyestuff Reptr. **29**, 400 (1940); Textile Research **10**, 453 (1940).

smoothness were investigated without success. Thus, except in such series as those illustrated above, the coefficient of friction may not be a direct indication of the smoothness of a fabric.

The usefulness of the coefficient of friction for evaluating fabric finishes is further illustrated by the results of measurements on a series of warp-knit rayon dress fabrics that were prepared by treating separate portions of the same grey fabric with 1-percent solutions of nine commercial finishing agents. Each finishing agent produced different effects with respect to the smoothness, softness, and pliability of the fabrics. The smoother, the softer, and the more pliable these particular fabrics, the more desirable they were for their intended use. The fabrics are listed in table 3, in groups, in the order of decreasing desirability as determined by three experts. The coefficients of kinetic friction obtained with the friction meter are given, together with values for flexibility and compressibility. Since the properties affecting the hand of these fabrics were integrated mentally by the experts evaluating them, and since a study of the results of the physical measurements indicated that a good quality in one property compensated for a poorer one in another, the results of the physical measurements were combined in the simplest ratio consistent with their relationship to the desirability of these fabrics. As shown in the table, the ratio combining all three measured values gives a better indication of the desirability of these fabrics than any one of the measured values alone or the ratio of the values of compressibility and flexibility.

TABLE 3.—*Correlation between the desirability of finish and several properties of warp-knit rayon dress fabrics*

Fabric designation	Desirability of finish	Coefficient of friction [1]	Flexibility [2] (torque, ergs/degree)	Compressibility [3]	$\frac{\text{Compressibility} \times 100}{\text{Flexibility}}$	$\frac{\text{Compressibility} \times 100}{\text{Flexibility} \times \text{coefficient of friction}}$
A	Excellent	0.39	19.6	0.278	1.42	3.64
B		.43	22.1	.254	1.15	2.67
C	Good	.40	20.9	.246	1.18	2.94
D		.42	21.6	.246	1.14	2.71
E		.44	21.6	.266	1.23	2.80
F	Fair	.46	20.9	.261	1.25	2.71
G		.48	19.4	.241	1.24	2.59
H	Poor	.41	26.7	.227	0.86	2.07
I		.44	24.4	.227	0.93	2.11

[1] Friction meter.
[2] Schiefer flexometer [4].
[3] Compression meter [5]. The quantities are proportional to the volume lost by the fabric upon changing the pressure on the fabric from 0.05 to 0.45 pound per square inch.

This suggests the possibility that values of the coefficient of friction, flexibility, and compressibility may give a means of distinguishing the differences of hand of series of similarly constructed fabrics. The choice of a method for combining the numerical values for these properties will depend upon the character of the hand desired, for the desired character of hand varies with such factors as the purpose for which the fabric is intended and current fad. Once a method is

devised for a given class of fabrics, however, then the hand of other fabrics of the class presumably may be determined from the results of measurements of the frictional, flexural, and compressional properties.

The studies on these and numerous other groups of fabrics lead to the following conclusions: The coefficient of friction contributes to the evaluation of smoothness but in itself is not always a measure of smoothness. For similar fabrics, where other properties are approximately the same, the fabric with the lower coefficient of friction is the smoother. The coefficient of friction, when considered with other properties affecting the hand of fabrics, may lead to an over-all evaluation of hand. A knowledge of frictional characteristics is necessary for the specification of finish.

VI. APPLICATIONS OF THE FRICTION METER

The friction meter has been applied to the testing of a wide variety of fabrics, including cotton percales, broadcloths, poplins, twills, and sateens; rayon crepes, twills, satins, and spun rayons of linen-like and challis-like finish; wool and mixed wool-rayon uniform shirtings and suitings; and knit fabrics including warp-knit rayon dress fabrics and silk and nylon hosiery. The ranges of values obtained for these fabrics are given in table 4.

TABLE 4.—*Range of coefficient of kinetic friction of different types and constructions of fabrics*

Types and constructions	Coefficient of kinetic friction
Cotton:	
80×80 percales	0.35 to 0.60
100×60 broadcloths	.33 to .56
100×40 poplins	.40 to .58
68×72 twills	.39 to .67
65×110 sateens	.34 to .49
Rayon:	
165×72 crepes	0.24 to 0.36
116×67 twills	.14 to .21
225×65 satins	.24 to .33
68×62 spun rayons:	
Linen-like	.66 to .74
Challis-like	.68 to .74
Wool and mixed wool-rayon:	
Uniform shirtings	0.78 to 1.03
Uniform suitings	.69 to 0.94
Knit fabrics:	
Warp-knit dress fabrics:	
Cuprammonium	0.39 to 0.48
Viscose	.26 to .30
Acetate	.34 to .52
Hosiery:	
3-thread silk, 30 turns, 42 gage	0.28 to 0.50
3-thread silk, high twist, 42 gage	.26 to .36
30-denier nylon, 51 gage	.22 to .31

The coefficient of friction can be used to evaluate the effectiveness of different finishing treatments. Table 5 gives results for five groups of fabrics, showing the effect on the coefficient of friction of calendering, concentration of finishing agent, kind of finishing agent, fiber construction, and laundering. The effects are in general large and indicate the applicability of the friction meter in evaluating and controlling textile processing.

The friction meter can also be used to measure the coefficient of

friction between two different fabric surfaces. Such measurements probably would be of use in evaluating the tendency of dresses and of underwear to "creep" when being worn.

TABLE 5.—*Effect of different treatments on coefficient of kinetic friction*

	Coefficient of kinetic friction	
Calendering—80×80 percale:		
Plain-finished	0.75	
Calendered	.49	
Concentration of finishing agent—80×80 print cloth:		
Untreated	.61	
1.0% finishing agent	.56	
1.5% finishing agent	.53	
2.0% finishing agent	.52	
Different finishing agents—silk stockings:		
Untreated	.30	
Softened	.28	
Delustered	.50	
Fiber composition—uniform suiting:		
All wool	.94	
50% wool-50% viscose	.69	
	Starch finish	Semi-permanent finish
Laundering—72×60 cotton sheeting:		
Before laundering	0.47	0.51
After first laundering	.79	.59
After second laundering	.77	.67
After fifth laundering	.73	.67

VII. REFERENCES

[1] George Rennie, *Experiments on the friction and the abrasion of the surfaces of solids*, Phil. Trans. Royal Soc. (London) **19,** Article 15, 143 (1929).
[2] A. A. Mercier, *Coefficient of friction of fabrics*, BS J. Research **5,** 243 (1930) RP196.
[3] J. A. Morrow, *The frictional properties of cotton materials*, J. Textile Inst. **22,** T245 (1931).
[4] H. F. Schiefer, *The Flexometer, an instrument for evaluating the flexural properties of cloth and similar materials*, BS J. Research **10,** 647 (1933) RP555.
[5] E. C. Dreby, *Physical methods for evaluating the hand of fabrics and for determining the effects of certain textile finishing processes*, Am. Dyestuff Reptr. **31,** P497 (1942).

WASHINGTON, July 12, 1943.

MATHEMATICAL TABLES

Attention is invited to a series of publications prepared by the *Project for the Computation of Mathematical Tables* conducted by the Federal Works Agency, Work Projects Administration for the City of New York, under the sponsorship of the National Bureau of Standards. The tables which have been made available through the National Bureau of Standards are listed below.

There is included in this list a publication on the hypergeometric and Legendre functions (MT15), prepared by the Bureau.

MT1. TABLE OF THE FIRST TEN POWERS OF THE INTEGERS FROM 1 TO 1000:

(1938) VIII+80 pages; heavy paper cover. Out of print.

MT2. TABLES OF THE EXPONENTIAL FUNCTION e^x.

The ranges and intervals of the argument and the number of decimal places in the entries are given below:

Range of x	Interval of x	Decimals given
—2.5000 to 1.0000	0.0001	18
1.0000 to 2.5000	.0001	15
2.500 to 5.000	.001	15
5.00 to 10.00	.01	12

(1939) XV+535 pages; bound in buckram, $2.00.

MT3. TABLES OF CIRCULAR AND HYPERBOLIC SINES AND COSINES FOR RADIAN ARGUMENTS:

Contains 9 decimal place values of sin x, cos x, sinh x and cosh x for x (in radians) ranging from 0 to 2 at intervals of 0.0001.
(1939) XVII+405 pages; bound in buckram, $2.00.

MT4. TABLES OF SINES AND COSINES FOR RADIAN ARGUMENTS:

Contains 8 decimal place values of sines and cosines for radian arguments ranging from 0 to 25 at intervals of 0.001.
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MT5. TABLES OF SINE, COSINE, AND EXPONENTIAL INTEGRALS, VOLUME I:

Values of these functions to 9 places of decimals from 0 to 2 at intervals of 0.0001.
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MT6. TABLES OF SINE, COSINE, AND EXPONENTIAL INTEGRALS, VOLUME II:

Values of these functions to 9, 10, or 11 significant figures from 0 to 10 at intervals of 0.001, with auxiliary tables.
(1940) XXXVII+225 pages; bound in buckram, $2.00.

MT7. TABLE OF NATURAL LOGARITHMS, VOLUME I:

Logarithms of the integers from 1 to 50,000 to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, $2.00.

MT8. TABLES OF PROBABILITY FUNCTIONS, VOLUME I:

Values of these functions to 15 places of decimals from 0 to 1 at intervals of 0.0001 and from 1 to 5.6 at intervals of 0.001.
(1941) XXVIII+302 pages; bound in buckram, $2.00.

[Continued on p. 4 of cover]

[Continued from p. 3 of cover]

MT9. TABLE OF NATURAL LOGARITHMS, VOLUME II:

Logarithms of the integers from 50,000 to 100,000 to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, $2.00.

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Logarithms of the decimal numbers from 0.0001 to 5.0000, to 16 places of decimals.
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MT12. TABLE OF NATURAL LOGARITHMS, VOLUME IV:

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MT13. TABLE OF SINE AND COSINE INTEGRALS FOR ARGUMENTS FROM 10 TO 100:
(1942) XXXII+185 pages; bound in buckram, $2.00.

MT14. TABLES OF PROBABILITY FUNCTIONS, VOLUME II:

Values of these functions to 15 places of decimals from 0 to 1 at intervals of 0.0001 and from 1 to 7.8 at intervals of 0.001.
(1942) XXI+344 pages; bound in buckram, $2.00.

MT15. The hypergeometric and Legendre functions with applications to integral equations of potential theory. By Chester Snow, National Bureau of Standards. Reproduced from original handwritten manuscript.

(1942) VII+319 pages; bound in heavy paper cover, $2.00.

MT16. TABLE OF ARC TAN X:

Table of inverse tangents for positive values of the angle in radians. Second central differences are included for all entries.

Range of x	Interval between successive arguments
0 to 7	0.001
7 to 50	.01
50 to 300	.1
300 to 2,000	1
2,000 to 10,000	10

(1942) XXV+169 pages; bound in buckram, $2.00.

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